



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Fresh Water Generation from Aquifer-Pressured Carbon Storage: Annual Report FY09

T.J. Wolery, R.D. Aines, Y. Hao, W. Bourcier, T.  
Wolfe, C. Haussman

December 1, 2009

## Disclaimer

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

## ANNUAL REPORT FEW0163

**Project Title: Fresh Water Generation from Aquifer-Pressured Carbon Storage**

**Principal Investigator: Roger D. Aines, Lawrence Livermore National Laboratory**

**Report Authors: Thomas J. Wolery, Roger D. Aines, Yue Hao, and William Bourcier (LLNL) and Thomas Wolfe and Chris Haussmann (PerLorica, Inc.)**

## EXECUTIVE SUMMARY

This project is establishing the potential for using brine pressurized by Carbon Capture and Storage (CCS) operations in saline formations as the feedstock for desalination and water treatment technologies including reverse osmosis (RO) and nanofiltration (NF). The aquifer pressure resulting from the energy required to inject the carbon dioxide provides all or part of the inlet pressure for the desalination system. Residual brine is reinjected into the formation at net volume reduction, such that the volume of fresh water extracted balances the volume of CO<sub>2</sub> injected into the formation. This process provides additional CO<sub>2</sub> storage capacity in the aquifer, reduces operational risks (cap-rock fracturing, contamination of neighboring fresh water aquifers, and seismicity) by relieving overpressure in the formation, and provides a source of low-cost fresh water to offset costs or operational water needs. This multi-faceted project combines elements of geochemistry, reservoir engineering, and water treatment engineering. The range of saline formation waters is being identified and analyzed. Computer modeling and laboratory-scale experimentation are being used to examine mineral scaling and osmotic pressure limitations. Computer modeling is being used to evaluate processes in the storage aquifer, including the evolution of the pressure field. Water treatment costs are being evaluated by comparing the necessary process facilities to those in common use for seawater RO.

There are presently limited brine composition data available for actual CCS sites by the site operators including in the U.S. the seven regional Carbon Sequestration Partnerships (CSPs). To work around this, we are building a “catalog” of compositions representative of “produced” waters (waters produced in the course of seeking or producing oil and gas), to which we are adding data from actual CCS sites as they become available. Produced waters comprise the most common examples of saline formation waters. Therefore, they are expected to be representative of saline formation waters at actual and potential future CCS sites. We are using a produced waters database (Breit, 2002) covering most of the United States compiled by the U.S. Geological Survey (USGS). In one instance to date, we have used this database to find a

composition corresponding to the brine expected at an actual CCS site (Big Sky CSP, Nugget Formation, Sublette County, Wyoming). We have located other produced waters databases, which are usually of regional scope (e.g., NETL, 2005, Rocky Mountains basins).

Produced waters have total dissolved salt content (TDS) ranging from a few hundred mg/L to about 400,000 mg/L. We have identified three major compositional families on the basis of dominant ionic composition: Na-Cl, Na-Ca-Cl, and Na-Cl-SO<sub>4</sub>. Seawater, a major focus of industrial RO, is Na-Cl brine with a TDS of about 35,928 mg/L. Na-Cl brines are very common and have a TDS range of a few hundred mg/L to about 350,000 mg/L. Na-Ca-Cl brines are also very common. They are usually more concentrated than seawater, with TDS values extending to 400,000 mg/L. Na-Cl-SO<sub>4</sub> brines are common only in certain geographic regions, mainly Rocky Mountain basins. TDS values fall at the low end, about 1000 mg/L to roughly 110,000 mg/L (for SO<sub>4</sub>/Cl mass ratio  $\geq 0.25$ ). In the United States, CCS operations are anticipated to be restricted to formations containing saline waters with TDS > 10,000 mg/L (USEPA proposed regulation: see: [http://www.epa.gov/safewater/uic/wells\\_sequestration.html#regdevelopment](http://www.epa.gov/safewater/uic/wells_sequestration.html#regdevelopment)).

The TDS of saline water is a key parameter in desalination. Higher TDS of feed water is associated with higher osmotic pressure (approximated by the van't Hoff equation), which requires more energy (pressurization) to drive water through an RO membrane. It is also associated with increased difficulties with mineral deposition (scaling), although specific chemistry (e.g., hardness) is also an important factor. The TDS of residual brine increases as fresh water is produced, increasing these problems, and there is some practical limit to how much fresh water can be extracted from the original feed water. In general, the higher the TDS of the feed water, the smaller the fraction of fresh water that can be obtained. We have analyzed data from the USGS Produced Waters database (Breit, 2002) for (a) the State of Wyoming and (b) the United States as a whole and found that saline formation waters in the TDS ranges 10,000-40,000 mg/L and 40,000-85,000 mg/L (discussed below as reasonable targets for conventional desalination) are abundant (more so in Wyoming than in the United States as a whole). In aggregate, they are more abundant (Wyoming) or as abundant (United States) as more concentrated brines (85,000-400,000 mg/L). A notable observation is that there is little shift toward more highly concentrated brines with increasing depth.

We are using a thermodynamic model based on Pitzer's equations (cf. Pitzer, 1991) to evaluate mineral deposition and osmotic pressure limitations for representative compositions from our brine catalog, including compositions from two CCS sites (Big Sky CSP, Sublette County, Wyoming and In Salah, Algeria). We have also performed more generic calculations for brines in the Na-Cl ("seawater") family. The thermodynamic model (Bechtel SAIC Company, 2007) was originally developed for use on the Yucca Mountain Project. It is based on the work of Pabalan and Pitzer (1987), Greenberg and Møller (1989), and many other sources, and supports

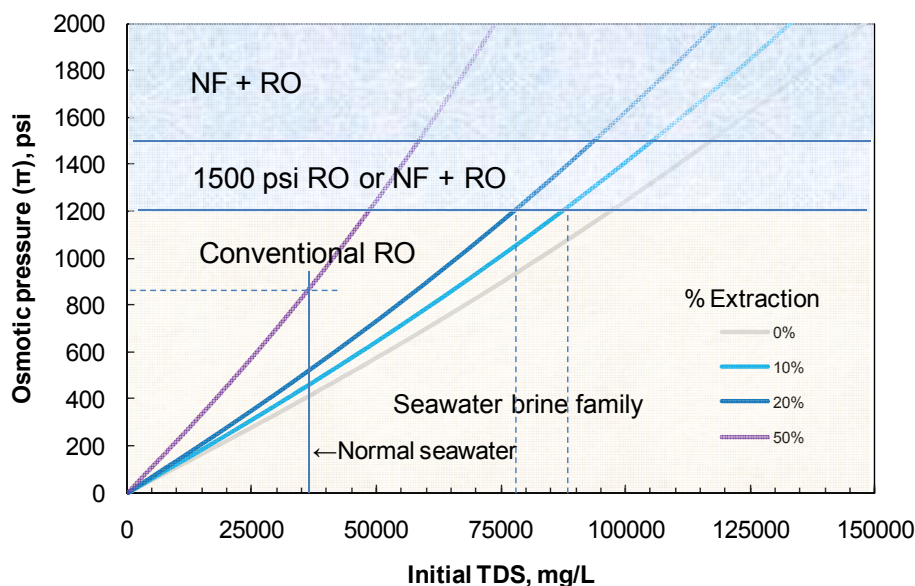
calculations over the temperature range 25-150°C. The in situ temperatures of many saline formation waters may be in the range 90-120°C due to the natural geothermal gradient, and the waters may largely retain these temperatures when brought to the surface. Model calculations are made using the EQ3/6 software package (cf. Wolery and Jarek, 2003).

The thermodynamic calculations simulate the extraction of fresh water, and predict the evolution of the residual brine. Model calculations assume desalination temperatures of 25-90°C, although we are focusing on 50°C due to materials and other issues (40°C is used in our cost estimate work). One important finding of our calculations is that the RO industry approximation for calculating the osmotic pressure (e.g., Dow, 2009, p. 90, eq. 15) is inaccurate for many saline formation water compositions. It works reasonably well for Na-Cl type brines up to about 120,000 mg/L TDS, and for any sufficiently dilute solution. It tends to under-predict osmotic pressure for Na-Ca-Cl brines and over-predict for Na-Cl-SO<sub>4</sub> brines. To address the range of saline formation waters, an accurate thermodynamic model is required. A second major finding is that osmotic pressure, not mineral precipitation, is the principal limiting factor for fresh water extraction. RO is a membrane-based process. It produces fresh water (which has an osmotic pressure of nearly zero) on one side of the membrane. The osmotic pressure difference (which must be overcome by applying a slightly greater pressure difference) is essentially the osmotic pressure of the feed or residual brine. When the membrane strength (typically 1200 psi) is exceeded, conventional RO cannot be applied (though a 1500 psi membrane now exists).

The following results for 50°C are illustrative. For a seawater brine (35,928 mg/L TDS), a 1200 psi membrane strength imposes a water extraction limit of 64%. This is consistent with industrial treatment of seawater (at somewhat lower temperature) to 40-50% extraction. The 1500 psi membrane would allow 71% extraction. For the Big Sky Carbon Sequestration Partnership site, the brine in the Nugget Formation is represented by “WY Sublette Co. #3” (10,000-11,000 ft. depth) from the USGS produced waters database (Breit, 2002). This is Na-Cl brine with a TDS of 85,926 g/L. The 1200 psi membrane permits only 7.5% water extraction, although the 1500 psi membrane increases this to a more useful 24%. Interestingly, for the same geographic site but in the underlying Tensleep Formation, the formation water (“WY Sublette Co. #2”, 13004-13092 ft. depth) is Na-Cl-SO<sub>4</sub> brine with TDS of only 24,501 mg/L. For this brine, the 1200 psi membrane would permit 86% water extraction (89% for the 1500 psi membrane). This would be a very attractive target for conventional RO. In contrast, saline formation water from the In Salah, Algeria CCS site (“Draft Krechba Report,” sample KB502Z, Na-Ca-Cl brine, 149,958 mg/L TDS) has an osmotic pressure > 1500 psi and thus cannot be treated by conventional RO.

Figure 1 shows the osmotic pressure versus initial TDS for various extents of water extraction (0, 10, 20, and 50%; one curve for each extent) for Na-Cl brines (“seawater brine family”), which is perhaps the most important type. Normal seawater (initial TDS of 35,928 mg/L) encounters the

50% extraction curve at about 830 psi, well within the limit of conventional RO. The 0% extraction curve encounters the 1200 psi limit of conventional RO at an initial TDS of about 98,000 mg/L, indicating that Na-Cl brines this concentrated cannot be treated by this method. The 10% extraction curve reaches the 1200 psi limit at an initial TDS of about 88,000 mg/L, while the 20% extraction curve reaches it at an initial TDS of about 77,000 mg/L. This suggests that for small extents of extraction, conventional RO can be useful for a fairly substantial fraction of subsurface brines. The range of RO could be extended with 1500 psi membranes. A multi-stage process such as NF + RO is required above 1500 psi, but might be used at lower pressure.



**Figure 1. Calculated osmotic pressure at 50°C of seawater family brine for various extents of water extraction (0, 10, 20, and 50%) as a function of initial TDS content. Normal seawater (35,928 mg/L) easily supports 50% extraction using conventional RO (1200 psi membranes). 98,000 mg/L initial TDS is an absolute limit to any extraction by conventional RO. 10% extraction is feasible by conventional RO up to initial TDS of about 88,000 mg/L, 20% extraction up to about 77,000 mg/L.**

We have made preliminary cost estimates for the desalination of pressurized formation brines from actual and possible future CO<sub>2</sub> sequestration sites. Once geologic storage operations at a site have increased the aquifer overpressure to about 500-1500 psi, brine can be extracted for treatment. Operation of such a system would require a series of brine extraction wells, a dedicated RO plant of size similar to plants used today in arid regions of the world, and brine reinjection wells to return the more concentrated residual brine to the aquifer.

The reservoir-pressurized process described here takes advantage of the pressurization of the field caused by CO<sub>2</sub> injection to drive desalination using RO. Thus, costs for fresh water

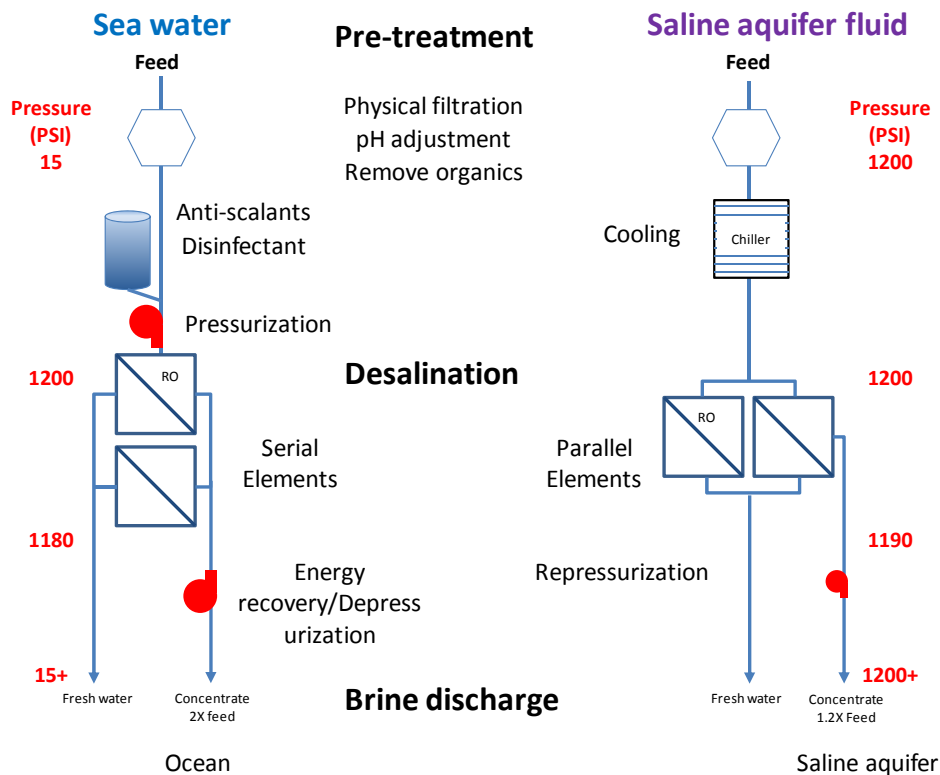
production by this method are expected to be significantly lower than for conventional seawater RO, for which energy costs can be 50% or more of total cost. Plant design for seawater processing is dominated by that energy cost, since water is taken into the plant at low pressure and residual brine must be discharged at low pressure. This dictates that as much fresh water as possible be extracted from a given volume of seawater, and drives process design toward multiple, sequential RO trains (in which residual brine is taken to sequentially higher pressure) to maximize energy efficiency. In the case of saline formation water where the inlet reservoir is already at high pressure and the residual brine will be returned to the reservoir at high pressure, the amount of fresh water extracted from the brine (% recovered) is no longer a critical parameter and it is feasible to use much simpler, single RO train systems. This simplification results in both cost savings and flexibility in plant design. That flexibility has only been summarily examined in this report and will be an important focus of next year's work. Processing saline formation brines also leads to some increased costs for the treatment plant, primarily the need for pressure-rated piping for the inlet and outlet systems and heat exchangers (because the brine is expected to be produced at temperatures above the working temperature range of RO membranes).

A typical 1 GW coal plant emits more than 7 million tons of carbon dioxide per year. A well-designed capture system might provide 6 million tons for sequestration. Sequestered at a depth of 10,000 ft, this CO<sub>2</sub> would displace about 7.5 million cubic meters of water, or a little less than six million gallons per day. Reverse osmosis treatment of that brine would produce about 6000 acre-feet of fresh water, which could serve the needs of 10,000 homes, irrigate 2000 acres of cropland, or provide half of the total fresh water usage of a typical 1 GW IGCC power plant.

Our analysis indicates that at this scale, RO plants for brines of 10,000-85,000 mg/L TDS can be built and operated for about half of the cost of seawater desalination. Producing fresh water at the six million gallon (about 18 acre feet) per day rate would cost about \$450 to \$600 per acre foot, with more saline brines resulting in the higher costs. This analysis includes all surface facilities, transfer pumps, and piping, but does not consider the cost of the brine extraction and reinjection wells. The number and design of these wells will be somewhat site dependent. Next year's work will include a conceptual evaluation based on representative sites from the CSP sites. Brines with TDS of 85,000-300,000 mg/L will require additional treatment steps that will be evaluated in next year's work. Combination of NF with RO is expected to be straightforward.

RO desalination of seawater is a fairly mature technology and provides a useful baseline. Figure 2 (left hand side) shows a schematic of the process, which consists of three main steps: (1) pre-treatment of the feed using one or more of physical filtration, coagulation, chemical sterilization, and contact with granular activated carbon (GAC); (2) reverse osmosis; and (3) permeate storage and distribution. The RO process is generally carried out in a spiral-wound tubular geometry in

order to achieve a large membrane surface area in a small volume. It also allows convenient replacement of fouled or aging membrane modules. The RO step is often carried out in two or three stages at successively higher pressures, the goal of which is to maximize water recovery while saving energy. Each stage after the first extracts additional fresh water from the residual brine provided by the previous stage. The operating pressure and membrane types of each stage are optimized for the salinity of the water being processed.



**Figure 2. Schematic comparison of desalination of seawater vs. desalination of saline formation waters.**

Seawater is uniform in major-ion composition worldwide, varying only about  $\pm 10\text{-}15\%$  in TDS. Biologically affected components such as calcium, silica, and phosphate may vary locally. Because of the general uniformity of feed water composition, designs of seawater RO systems tend to be similar to one another, with the major influencing factors being feed temperature and feed water quality with respect to concentrations of organics and suspended solids, which are a function of the feed source. Biological film fouling is especially problematic for seawater RO because the chemicals commonly used to kill micro-organisms, such as chlorine and ozone, will damage the polyamide layer on RO membranes.

Saline formation waters are much more diverse in composition, as has been noted previously. They vary in dominant-ion family (generally Na-Cl, Na-Ca-Cl, and Na-Cl-SO<sub>4</sub>), TDS, pH,



relative amounts of hardness (Ca +Mg) to alkalis (Na +K), alkalinity, and minor components. The design of systems to desalinate such waters must adapt to this variability.

Figure 2 (right side) shows how the RO process for saline formation waters differs from the standard process for seawater (left side). The major differences are:

1. The need for a heat-exchanger (chiller) prior to membrane treatment to cool the fluids to the working range of standard water treatment components (<60°C or 140°F)
2. Less need for filtration and pre-treatment due to the better quality of fluid in terms of total suspended solids (TSS) and less biological/organic matter
3. Lack of need for a high-pressure pump to pressurize the feed water (resulting in major cost savings relative to conventional seawater RO)

Saline formation waters with TDS > 85,000 mg/L may be amenable to membrane desalination using an NF pretreatment system for the removal of hardness and to reduce the overall TDS. NF allows much of the salinity from the feed water to pass to the permeate (consequently, the osmotic pressure difference and operating pressure drop across the membrane is not so great), while tending to retain divalent cations such as calcium on the feed/residual brine side. The permeate water from the NF step (or steps), still under high pressure, would then be fed to a modified seawater RO system as described in this report. The total amount of fresh water recovered via a NF + RO process would likely be < 25%. The technical and cost evaluation of NF + RO is beyond the scope of this year's study, but may be included in subsequent work.

Using the NUFT code (Nitao 2000a, 2000b), we have conducted preliminary simulations of the effect on the reservoir pressure field of CO<sub>2</sub> injection with and without brine production. Our results for the case of injection with no brine production are qualitatively consistent with previously reported results (e.g., Birkholzer and Zhou, 2009; Birkholzer et al., 2009), which show that the overpressure field expands well out from the body of injected supercritical CO<sub>2</sub>. Our simulations indicate that brine production reduces the peak overpressure, in this particular model system from ~65 bars to ~34 bars. However, there is a tendency for the supercritical CO<sub>2</sub> plume to migrate towards the brine production well.

Several reservoir modeling issues remain to be addressed, such as the optimum number and configuration of wells (including at least one residual brine reinjection well) and rates of injection and production. A brine production well (which produces a surrounding field of underpressure) must be emplaced so as to have a beneficial effect on the overall pressure field, but cannot be so close that injected CO<sub>2</sub> migrates into it. A brine reinjection well produces a surrounding field of overpressure, which also needs to be analyzed. Migration of residual brine to a brine production well needs to be avoided. The effect of limiting formation overpressure on

preventing leakage from the storage formation and on controlling unwanted geomechanical effects needs to be evaluated. These issues will be explored in the coming year.

Our initial conclusions are encouraging:

1. Many saline formation waters such as those found in Wyoming are amenable to conventional RO treatment. We have looked at Na-Cl brine from the Nugget Formation at the Big Sky Carbon Sequestration Partnership site in Sublette County, Wyoming. Here 7.5- 24% removal with conventional RO is realistic; higher removal appears achievable with NF. The lower TDS Na-Cl-SO<sub>4</sub> brine from the underlying Tensleep Formation would support >80% removal with conventional RO.
2. Brines from other proposed sequestration sites can now be analyzed readily. An accurate osmotic pressure curve appropriate to these brines can be used to evaluate cost and equipment specifications. Next year we will consider more of the United States CSP site brines as analyses from Phase 3 operations become available.
3. We have examined a range of saline formation water compositions relevant or potentially relevant to CCS and noted the principal compositional trends pertinent to evaluating the feasibility of fresh water extraction. We have proposed a general categorization for the feasibility of the process based total dissolved solids (TDS):
  - 10,000–40,000 mg/L TDS: Standard RO with  $\geq 50\%$  recovery
  - 40,000–85,000 mg/L TDS: Standard RO with  $\geq 10\%$  recovery; higher recovery possible using 1500 psi RO membranes and/or multi-stage incremental desalination likely including NF (nanofiltration)
  - 85,000–300,000 mg/L TDS: Multi-stage process (NF + RO) using process design that may differ significantly from seawater systems
  - > 300,000 mg/L TDS brines: Not likely to be treatable

Brines in the 10,000-85,000 mg/L TDS range appear to be abundant (geographically and with depth) and could be targeted in siting CCS operations.

4. Cost of RO treatment of 10,000-85,000 TDS brines may be half that for conventional seawater plants. An innovative parallel low-recovery approach is proposed for saline formation waters in the upper part of this TDS range.
5. Withdrawing pressurized brine can have very beneficial effects on reservoir pressure (helping to avoid leakage and undesirable geomechanical effects), while increasing total available storage capacity.

## PROJECT OBJECTIVES

Our objective is to establish the feasibility of using saline formation waters pressurized by Carbon Capture and Storage (CCS) operations as the feedstock for desalination and water treatment technologies including reverse osmosis (RO) and nanofiltration (NF). The aquifer pressure resulting from the energy required to inject the carbon dioxide provides all or part of the inlet pressure for the desalination system. Residual brine is reinjected into the formation at net volume reduction, such that the volume of fresh water extracted balances the volume of CO<sub>2</sub> injected into the formation. This process provides additional CO<sub>2</sub> storage capacity in the aquifer, reduces operational risks (cap-rock fracturing, contamination of neighboring fresh water aquifers, and seismicity) by relieving overpressure in the formation, and provides a source of low-cost fresh water to offset costs or operational water needs. This multi-faceted project combines elements of geochemistry, reservoir engineering, and water treatment engineering. The range of saline formation waters is being identified and analyzed. Computer modeling and laboratory-scale experimentation are being used to examine mineral scaling and osmotic pressure limitations. Computer modeling is being used to evaluate processes in the storage aquifer, including the evolution of the pressure field. Water treatment costs are being evaluated by comparing the necessary process facilities to those in common use for seawater RO.

## BRINE GEOCHEMISTRY AND GEOCHEMICAL MODELING

The original intent of this project was to focus on brine compositions specific to actual CCS sites disposing CO<sub>2</sub> into saline formations, including sites of the seven U.S. regional Carbon Sequestration Partnerships (CSPs). The expectation was that new samples of brine would be obtained from these sites, and that sampling and analysis would be state-of-the-art in order to overcome various well-known problems with historical chemistry data (e.g., volatile loss, mineral precipitation, incomplete analysis). It is anticipated that examples of new state-of-the-art data will become increasingly available. However, there are presently limited brine composition data obtained at actual CCS sites by the site operators.

To work around this, we are building a “catalog” of compositions representative of “produced” waters (waters produced in the course of seeking or producing oil and gas), to which we are adding data from actual CCS saline aquifer disposal sites as they become available. Produced waters comprise the most common examples of saline formation waters. Therefore, they are expected to be representative of saline formation waters at actual and potential future CCS disposal sites. We are using a produced waters database (Breit, 2002) covering most of the United States compiled by the U.S. Geological Survey (USGS). We note that the geographic

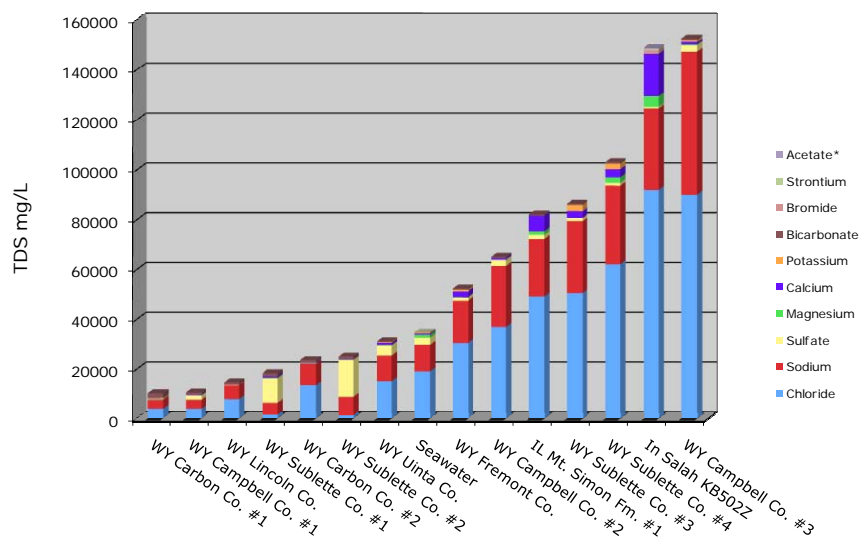
coverage of this database is skewed toward certain states and regions. For example, there is an abundance of data for the states of Texas, Wyoming, Oklahoma, and Kansas, while there are relatively few data for Ohio, Pennsylvania, New York, and West Virginia. The USGS database contains data in files organized by state or by a group of states, and also includes one data file for the United States as a whole. To date, we have primarily focused on the Wyoming and whole United States data. In one instance to date, we have used this database to find a composition corresponding to the brine expected at an actual CCS site (Big Sky CSP, Nugget Formation, Sublette County, Wyoming). We have located additional produced waters databases, which are usually of regional scope (e.g., NETL, 2005, Rocky Mountains basins, which appears to largely overlap with the USGS database for Wyoming).

Produced waters have total dissolved salt content (TDS) ranging from a few hundred mg/L to about 400,000 mg/L. Looking mainly at the Wyoming and whole United States datasets from the USGS database, we have identified three major compositional families on the basis of dominant ionic composition: Na-Cl, Na-Ca-Cl, and Na-Cl-SO<sub>4</sub>. Seawater, a major focus of industrial RO, is Na-Cl brine with a TDS of about 35,928 mg/L. Na-Cl brines are very common and have a TDS range of a few hundred mg/L to about 350,000 mg/L. Na-Ca-Cl brines are also very common. They are usually more concentrated than seawater, with TDS values extending to 400,000 mg/L. Na-Cl-SO<sub>4</sub> brines are common only in certain geographic regions, mainly Rocky Mountain basins. TDS values fall at the low end, about 1000 mg/L to roughly 110,000 mg/L (for SO<sub>4</sub>/Cl mass ratio  $\geq 0.25$ ). In the United States, CCS operations are anticipated to be restricted to formations containing saline waters with TDS > 10,000 mg/L (USEPA proposed regulation: see: [http://www.epa.gov/safewater/uic/wells\\_sequestration.html#regdevelopment](http://www.epa.gov/safewater/uic/wells_sequestration.html#regdevelopment)).

In building our brine catalog, we began by choosing specific examples of known brine types from the Wyoming part of the USGS database. This was more convenient to use than the whole United States dataset, owing to the higher relative abundance of Na-Cl-SO<sub>4</sub> brines. This did, however, limit us to examples with TDS not much exceeding 300,000 mg/L TDS. For examples of still more concentrated brines, we would need to draw from other datasets. However, treatment of brines with TDS above 300,000 mg/L is likely to be impractical. We chose only representative examples of brines with TDS > 10,000 mg/L in deference to the proposed USEPA regulation. We then added seawater as a reference, a reported Mt. Simon formation (Illinois Basin) brine, and brine from the In Salah, Algeria carbon sequestration site.

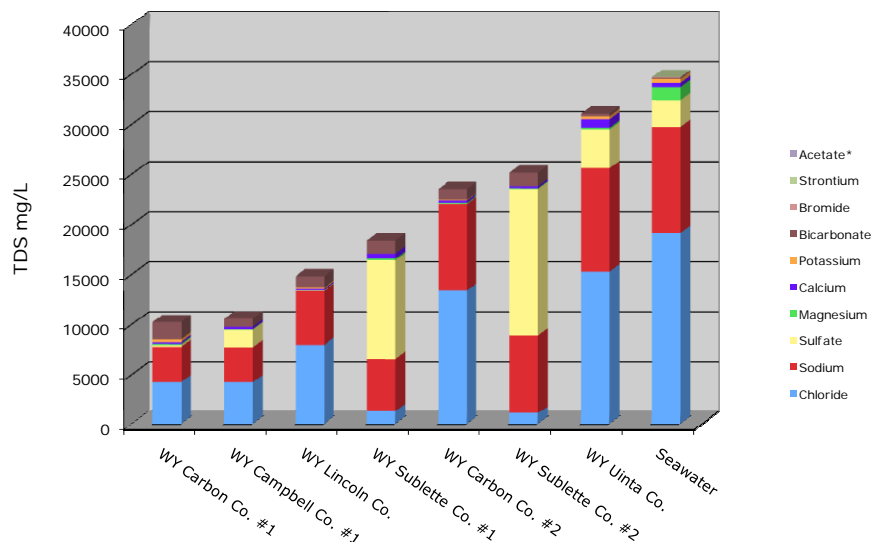
Figure 3 shows the part of the catalog extending to 160,000 mg/L TDS. This would be expected to cover most of the most easily treatable range. Seawater (35,928 mg/L TDS) is located near the middle. It represents the Na-Cl brine or “seawater” family. The Na-Ca-Cl brines (mostly more concentrated than seawater) are exemplified by “IL Mt. Simon Fm. #1” and “In Salah KB502Z”. The Na-Cl-SO<sub>4</sub> brines (mostly less concentrated than seawater) are exemplified by WY Sublette

Co. #1 and WY Sublette Co. #2 (from the Tensleep formation). Figure 4 shows these brines in greater detail (it depicts only the part of the catalog extending to 40,000 mg/L TDS).



**Figure 3. Catalog of subsurface brine compositions (brines with TDS > 160,000 mg/L are not shown).**

\*Acetate includes related organic acid anions such as propionate).



**Figure 4. Catalog of subsurface brine compositions (lower range only, brines with TDS > 40,000 mg/L are not shown).** \*Acetate includes related organic acid anions such as propionate).

The brine catalog is not designed to represent frequency. We examined the frequency issue using the USGS Wyoming database, which includes data for 9726 brine samples. We excluded samples lacking data for TDS and/or depth (as “UPPERDEPTH”), resulting in 8530 usable instances. Then we computed histograms for all usable brine samples produced from at or below various depths. Histograms for  $\geq 3000$  ft. and  $\geq 11,000$  ft. depths are shown here in Figure 5 and Figure 6, respectively. This analysis indicates that Wyoming brines with TDS in the range 10,000-40,000 mg/L are common at all depths examined.

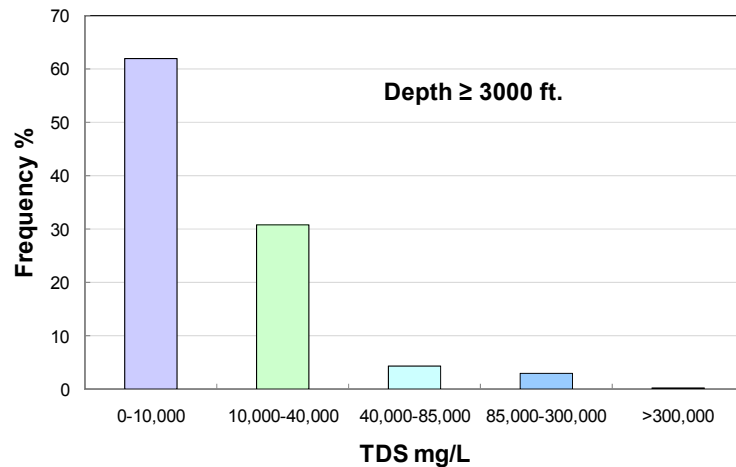


Figure 5. TDS distribution for Wyoming brines produced from depths  $\geq 3000$  ft.

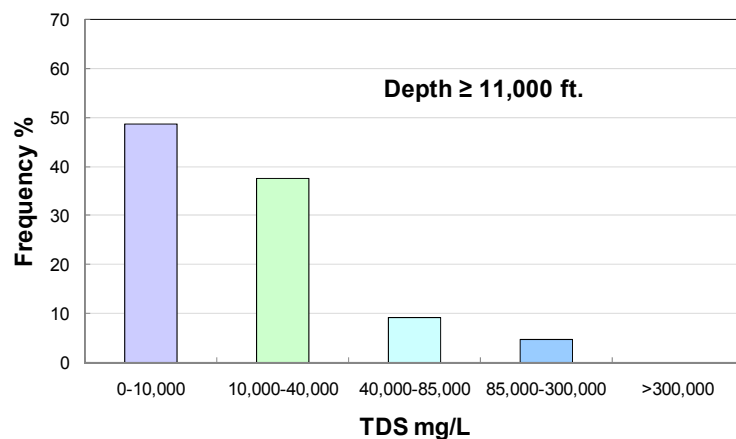


Figure 6. TDS distribution for Wyoming brines produced from depths  $\geq 11,000$  ft.

A similar analysis was conducted for the USGS whole United States database of produced waters. This database includes results for 58,706 brine samples, including the Wyoming samples. We again excluded samples lacking TDS or depth data, leaving 47,821 useable instances. Histograms for  $\geq 3000$  ft. and  $\geq 11,000$  ft. depths are shown in Figure 7 and Figure 8, respectively. Here brines in the TDS 10,000-40,000 mg/L and 40,000-85,000 mg/L ranges are abundant and there is again little change in the in the distribution of TDS with depth. For the whole United States, brines in the 0-10,000 mg/L and 10,000-40,000 mg/L TDS ranges are less abundant than in Wyoming, but brines in the range 40,000-85,000 mg/L TDS are more abundant.

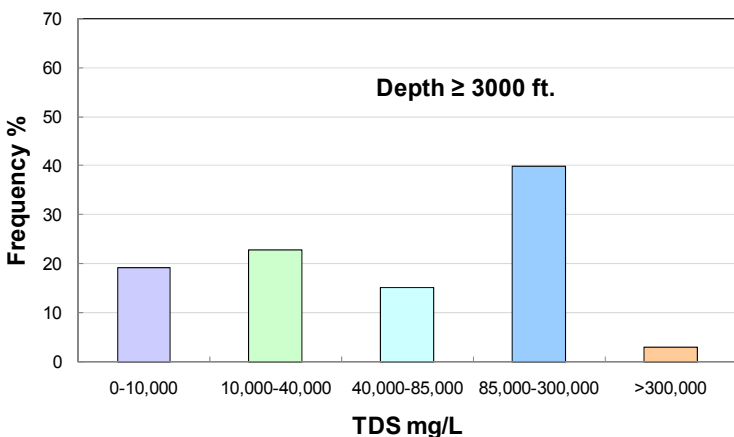


Figure 7. TDS distribution for United States brines produced from depths  $\geq 3000$  ft.

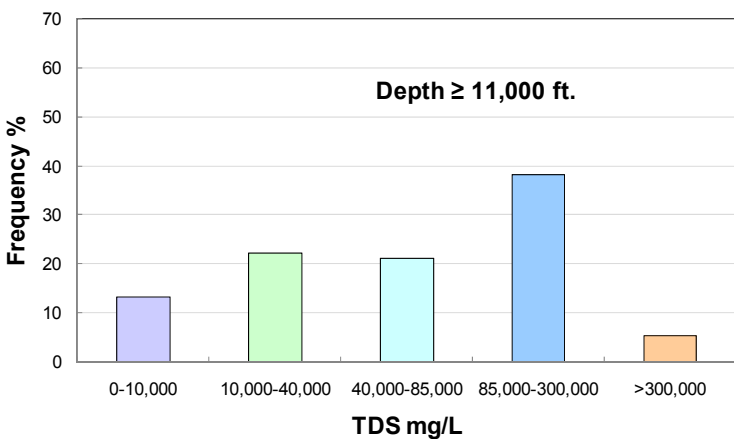


Figure 8. TDS distribution for United States brines produced from depths  $\geq 11,000$  ft.

The brine catalog is a work in progress. We are continuing to add to and refine it using data from other sites and regions. We are also continuing limited analysis of produced water databases to better understand frequency issues.

A thermodynamic model (Bechtel SAIC Company, 2007) based on Pitzer's equations (cf. Pitzer, 1991) has been used to evaluate the effects of reverse osmosis (RO) treatment of subsurface brines representative of potential CO<sub>2</sub> injection sites. The model was originally developed for use on the Yucca Mountain Project. It is based on the work of Pabalan and Pitzer (1987), Greenberg and Møller (1989), and many other sources, and supports calculations over the temperature range 25-150°C (the in situ temperatures of many saline formation waters may be in the range 90-120°C due to the natural geothermal gradient). Model calculations are made using the EQ3/6 software package (cf. Wolery and Jarek, 2003). An alternative thermodynamic model based on Extended UNIQUAC theory (cf. Thomsen 1997, 2005) is also available in EQ3/6. Other usage suggests that it would have given essentially the same results for the systems modeled here.

The thermodynamic calculations simulate the extraction of fresh water, and predict the evolution of the residual brine. Featured results for our purposes include the evolution of the osmotic pressure (which is related to the thermodynamic activity of water) and mineral precipitation driven by increasing solute content. The model calculations assume desalination temperatures of 25-90°C, although we are focusing on 50°C due to materials and other issues. We note that 40°C is used in our cost estimate work. The temperature dependence of the thermodynamic calculations is such that this difference is not very significant.

We first discuss calculations for two cases, a "seawater" brine and a representative brine from the Big Sky CSP site in Sublette County, Wyoming ("WY Sublette Co. #3). The latter is significantly higher in TDS (total dissolved solutes) than the former: 85,926 g/L, versus 35,928 g/L. Seawater is the brine most commonly treated by RO today, and much of the present technology and practical knowledge base pertinent to treatment of brines is focused on it. Some subsurface brines are similar in composition to seawater (as shown in Figure 3 and Figure 4), and many subsurface brines are thought to have been derived from it. Thus, seawater is a useful reference. Subsurface "seawater" brine would have some differences from surface seawater. For example, it would not likely be supersaturated with respect to calcium and magnesium carbonate phases, as is surface seawater, and it would not contain the same biological or organic components. The representative brine from the Big Sky CSP site is based on historical data for brines produced from the Nugget Formation at depths of about 10,000-11,000 ft. Matching direct measurements of subsurface temperatures were not available, but estimates of the local geothermal gradient suggest in situ temperatures in the range 72-104°C.



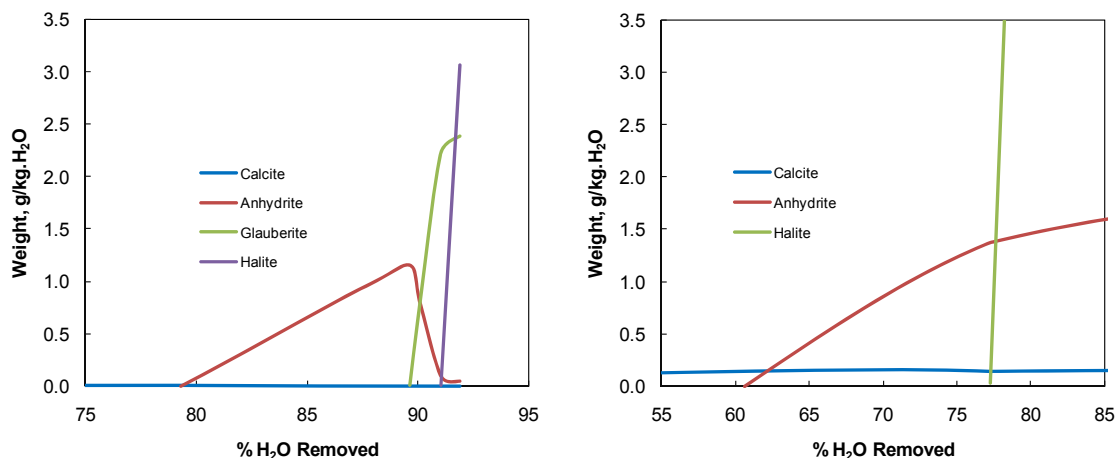
Results of the calculations simulating the evolution of the residual fluids were obtained. Most of the calculations were made for batch systems, though some were also made for flow-through systems (in which cases precipitated minerals become separated from the residual fluid and cannot later back-react). Only the results for 50°C batch simulations will be shown here. As was noted previously, this is a likely treatment temperature.

Figure 9 shows the calculated mineral precipitation for the seawater brine and the Big Sky CSP site brine (WY Sublette Co. #3) as a function of % H<sub>2</sub>O removed. Only the upper ranges in which major mineral precipitation occurs are shown. Minor calcite (CaCO<sub>3</sub>) appears near the start of the water removal process and persists, but this is not very significant quantitatively. Anhydrite (CaSO<sub>4</sub>) is the first major precipitate, appearing at 79% H<sub>2</sub>O removed in the case of the seawater brine, and at 62% H<sub>2</sub>O removed in the case of the Big Sky CSP brine. In the seawater case, anhydrite is replaced at higher extent of water removal by glauberite (Na<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>). Glauberite does not appear in the Big Sky CSP brine case. The calculations are stopped shortly after halite (NaCl) begins to precipitate. At higher extents of H<sub>2</sub>O removed, the amount of halite would be very substantially higher than the range shown in Figure 9. Once halite starts to precipitate, brine treatment is essentially infeasible. At other temperatures, calcite and halite behave similarly. However, at lower temperature the precipitation of anhydrite (the principal sulfate) shifts right to higher extent of water removed, while at higher temperature it shifts left (to only 8% water removed for the Big Sky brine at 90°C, to 45% water removed for the seawater brine at the same temperature).

The precipitation of sulfates (e.g., anhydrite, glauberite) would be problematic in a treatment process. Calculations such as those represented in Figure 9 are therefore useful in planning a treatment process. If it were desired to push the treatment process into the range in which sulfate minerals precipitate, mitigation measures (e.g., to inhibit precipitation, or to inhibit sticking of precipitates to the treatment apparatus) or alternative treatment (e.g., nanofiltration) would be necessary.

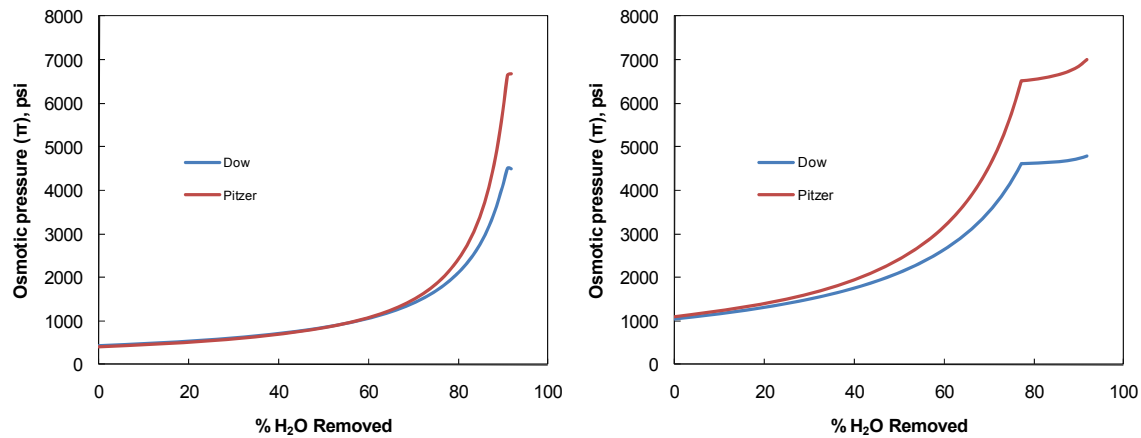
RO treatment of seawater in current industrial practice generally does not exceed 60% H<sub>2</sub>O removed, although at lower temperature the precipitation of sulfates is displaced toward even higher extent of H<sub>2</sub>O removed than is shown in Figure 9 (left). Something other than the precipitation of sulfates is the limiting factor in conventional RO treatment of seawater. This is likely due a combination of membrane limitations (discussed below), energy requirements, the ready availability of “fresh” seawater at seawater RO facilities, and potential environmental concerns regarding disposal of the residual brine. The limit of water extraction is nonetheless being pushed upward. In the case of an equivalent subsurface brine produced at a CO<sub>2</sub> sequestration site, the overall analysis supporting a feasible or optimal extraction of freshwater would be subject to a somewhat different set of constraints. A higher degree of freshwater

extraction, or equivalently a more concentrated residual brine, could well be supportable. This is especially true if the subsurface pressure due to CO<sub>2</sub> injection can be used to provide part or all of the pressure needed to run the reverse osmosis (or nanofiltration) process, and an appropriate value is placed on limiting the pressure in the subsurface injection formation (e.g., maintaining a safety margin for caprock integrity).



**Figure 9. Predicted mineral precipitation as a function of water removal due to reverse osmosis at 50°C in a batch system. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site. Minor calcite (CaCO<sub>3</sub>) precipitates at the start (not shown) and persists. The calculations are stopped shortly after halite (NaCl) begins to precipitate. Water treatment at this point becomes infeasible.**

A key factor in evaluating the energetics is the minimum pressure that must be applied to drive the process. The thermodynamic limit is the osmotic pressure. For high ionic strength brines, an accurate value can only be obtained using a thermodynamic model, such as ours based on Pitzer's equations. In this approach, the osmotic pressure is obtained from the thermodynamic activity of water using first principles. In the literature, the osmotic pressure is often calculated from the van't Hoff equation, which is a limiting approximation valid only in relatively dilute solutions. The Dow model used in industrial practice is essentially equivalent to the van't Hoff equation (it uses molality for the total solute concentration instead of molarity). Figure 10 shows the osmotic pressure results obtained from our calculations using the Pitzer model, compared with results from the Dow model. The Dow model underpredicts the osmotic pressure above 60% water removed for the seawater brine, and above only 20% water removed for the Big Sky CSP brine (WY Sublette Co. #3). At high extent of water removal, the underprediction becomes severe, and only results based on an accurate thermodynamic model should be used. At higher temperature, the osmotic pressure increases nearly linearly with the absolute temperature (exactly linearly for the Dow model). This dependency is not strong in the range of absolute temperature of interest here.

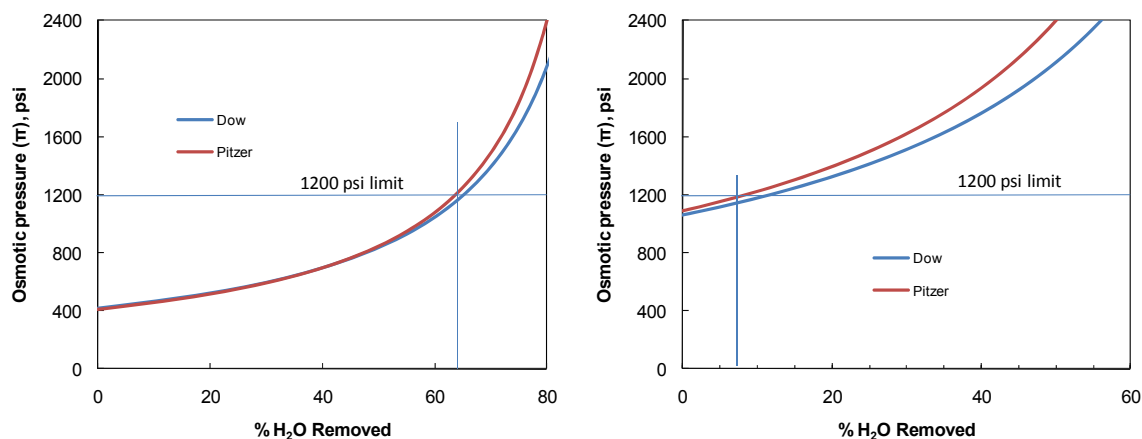


**Figure 10. Predicted osmotic pressure in residual brine as a function of water removal due to reverse osmosis at 50°C in a batch system. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site . The “Pitzer” curves show the osmotic pressure as obtained from the activity of water calculated from a thermodynamic model using Pitzer’s equations. The Dow model is a minor variation on the classic van’t Hoff equation, neither of which is generally valid in high ionic strength brines.**

RO works by applying a pressure difference across the membrane. Thermodynamically, the pressure difference ( $\Delta p$ ) between feed/residual brine and permeate solution must overcome the osmotic pressure difference ( $\Delta \pi$ ) between the two solutions. The ideal permeate would be pure water, which would have an osmotic pressure of zero. In practice this is not quite achievable, but nearly so. Thus, the osmotic pressure of the feed or residual brine approximately equates to the minimum pressure difference to make the process work. To obtain a good flux, a somewhat greater pressure difference is normally applied. In theory, greater water extraction can be obtained by applying enough pressure on the feed or residual brine side to overcome whatever resistance is applied by the brine’s osmotic pressure. Real membranes, however, can only withstand so much pressure. Until recently, RO membranes were limited to a pressure difference of 1200 psi. New membranes are rated to withstand 1500 psi. For consistency with our economic analysis (given later in this report), we will emphasize the more conventional value of 1200 psi.

Figure 11 shows the effect of a membrane strength of 1200 psi on conventional RO at 50°C of the seawater brine and the representative brine (WY Sublette Co. #3) near the Big Sky CSP site. The information is essentially that given in Figure 10, although the scale has been changed and the membrane strength is marked. For the seawater brine, the osmotic pressure reaches the conventional membrane strength of 1200 psi at about 64% water extraction. For the more concentrated Wyoming brine, this condition occurs at about 7.5% water extraction. What this means is that if higher extraction is required, it is necessary to apply a somewhat less

conventional treatment methodology. Using a higher membrane strength of 1500 psi would help, increasing these results to 71% and 24%, respectively.

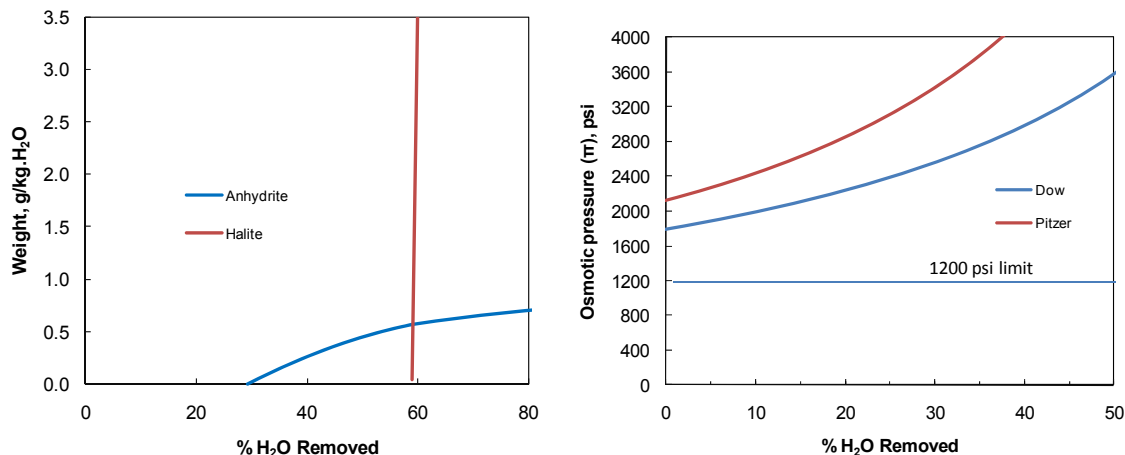


**Figure 11. Predicted osmotic pressure in residual brine as a function of water removal due to reverse osmosis at 50°C in a batch system, showing the effective of a maximum membrane strength of 1200 psi. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site .**

Achieving a higher level of extraction (beyond the limit for direct production of high-quality permeate for a given membrane strength) is possible if desalination takes place incrementally. The idea here is to raise the osmotic pressure on the permeate side so that the osmotic pressure difference is kept within the membrane strength. The salty permeate (less salty than the feed or residual brine) then becomes the feed to a subsequent RO step. A final RO step produces high-quality permeate. There are several ways to accomplish this staged RO process. Perhaps the least unconventional is to use a nanofiltration (NF) membrane, which preferentially rejects highly charged anions, notably sulfate. NF membranes produce a relatively salty permeate, but do so under pressure differences of only a few hundred psi. Permeate from an NF step can be fed into a subsequent NF step to produce a less concentrated permeate. A “high flux” RO membrane can be run at “low flux,” which will also produce a salty but less concentrated permeate. Finally, there is also the possibility of borrowing from forward osmosis methods and using a carrier electrolyte such as ammonium carbonate on the permeate side. The resulting permeate would be treated in a subsequent step to regenerate the carrier electrolyte. We note that the term “staged RO” is also used to refer to a process in which residual brine from an RO step is taken to a higher pressure and then treated in subsequent step. Both forms of “staging” could be used in a brine treatment process.

The In Salah KB502Z brine is a good example of a substantially more concentrated brine (149,958 mg/L TDS). Results are shown in Figure 8. The mineral precipitation suggests that water extraction of 58% might be achievable. However, the osmotic pressure is a more limiting

factor. The starting brine (feed composition) has an osmotic pressure that already exceeds the conventional 1200 psi membrane strength (as well as the more advanced 1500 psi value). Therefore, a staged treatment process would be required to extract any freshwater, and the fraction of extracted water would likely not be high, perhaps 25% at most.

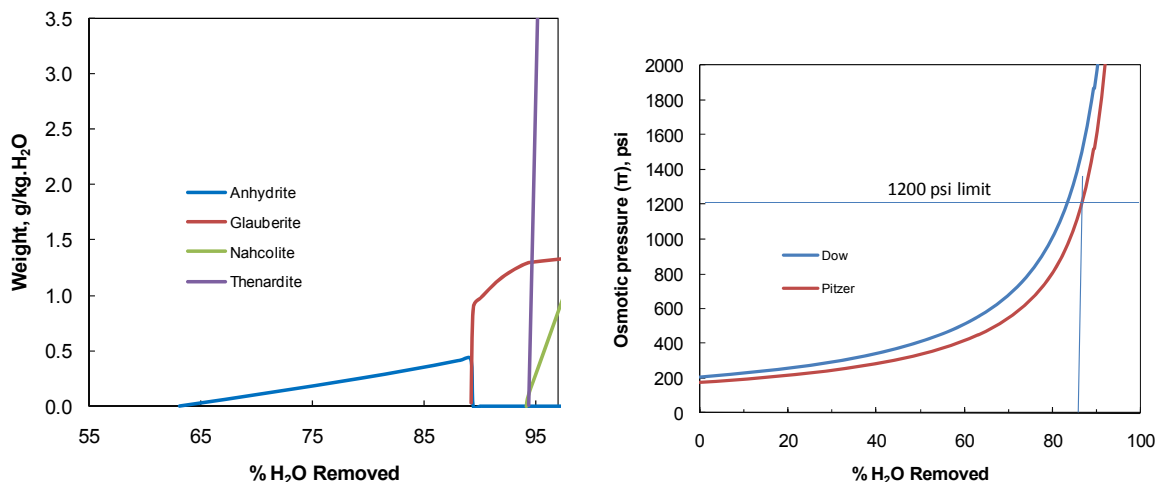


**Figure 12. Calculated results for reverse osmosis at 50°C of In Salah KB502Z brine in a batch system. Left: mineral precipitation. Right: osmotic pressure (only shown to 50% water removal).**

A very contrasting picture appears from calculations for WY Sublette Co. #2 brine, which is a sodium sulfate-sodium chloride brine (from the Tensleep Formation) with 24,501 mg/L TDS (less than the TDS of seawater). Results are shown in Figure 9. They suggest that mineral precipitation is manageable to at least 89% water extraction. At 94% water extraction, thenardite ( $\text{Na}_2\text{SO}_4$ ) precipitation is a definite limiting factor. Here thenardite plays the role played by halite in the brine examples discussed previously. The osmotic pressure does not achieve the 1200 psi limit until about 86% extraction (89% for a 1500 psi limit). It appears that very conventional RO treatment of this brine could easily achieve >80% extraction. Note that for this brine, the thermodynamic (“Pitzer”) estimation of the osmotic pressure is generally less than what is predicted by the Dow model. That is the reverse of what was seen for the sodium chloride and sodium chloride-calcium chloride brines.

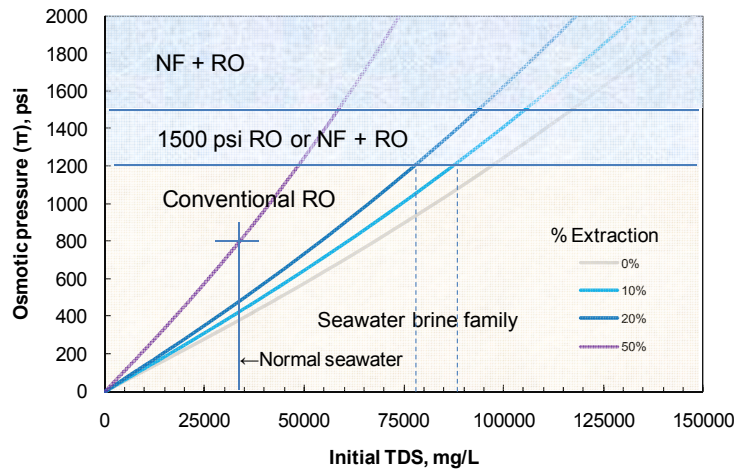
Because many of the examples of produced waters are members of the seawater brine family (defined as subsurface waters compositionally equivalent to diluted or concentrate seawater), it is useful to provide a special focus on this group. Figure 14 shows the osmotic pressure versus initial TDS for various extents of water extraction (0, 10, 20, and 50%; one curve for each extent). Normal seawater (initial TDS of 35,928 mg/L) encounters the 50% extraction curve at about 800 psi, well within the limit of conventional RO. On the other hand, the 0% extraction curve encounters the 1200 psi limit of conventional RO at an initial TDS of about 98,000 mg/L.

One may conclude that for brines in this family, this concentration marks the theoretical limit for treatment by conventional RO. Brines exceeding that limit require less conventional RO (1500 psi membranes) or NF + RO to obtain any extent of water extraction. On the other hand, the 10% extraction curve hits the 1200 psi limit of conventional RO at an initial TDS of about 88,000 mg/L, and the 20% extraction curve hits this limit at an initial TDS of about 77,000 mg/L. This suggests that for small extents of extraction, conventional RO can be useful for a fairly substantial fraction of likely subsurface brines (see Figure 5 and Figure 6 for Wyoming, and Figure 7 and Figure 8 for the United States as a whole).



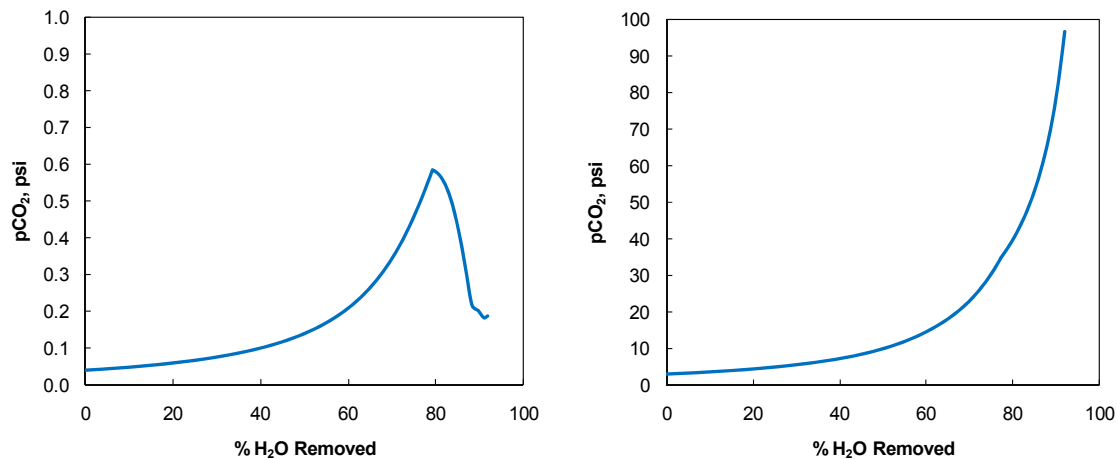
**Figure 13. Calculated results for reverse osmosis at 50°C of WY Sublette Co. #2 brine in a batch system. Left: mineral precipitation. Right: osmotic pressure.**

The calculations presented previously in this section do not account for potential transfer of components other than water through the treatment process. CO<sub>2</sub> pressures would build up in the residual brine, and CO<sub>2(aq)</sub> (or carbonic acid) would readily pass through a treatment membrane. This could alter the chemistry of the residual brine. A likely result of this would be calcite precipitation (more substantial than shown in Figure 4, for example) at or near the membrane surface. Such a process can be addressed by our modeling technology, but results are not included here. Figure 15 shows the buildup of CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) ignoring CO<sub>2</sub> passage through the membrane. The primary thing to note is that the scales are quite different between the seawater brine and the WY Sublette Co. #3 (Big Sky CSP site) brine. There is a small buildup of pCO<sub>2</sub> in the seawater case, followed by a decline once anhydrite starts to precipitate. The consequences of CO<sub>2</sub> passage through a membrane would be relatively small. There is a much larger buildup in the case of the WY Sublette Co. #3 brine, and there is no decline in pCO<sub>2</sub>, despite the precipitation of anhydrite. The behavior in these systems is not simple, and is



**Figure 14. Calculated osmotic pressure at 50°C of seawater family brine for various extents of water extraction (0, 10, 20, and 50%) as a function of initial TDS content. Normal seawater (35,928 mg/L) easily supports 50% extraction using conventional RO (1200 psi membranes). 98,000 mg/L initial TDS is an absolute limit to any extraction by conventional RO. 10% extraction is feasible by conventional RO up to initial TDS of about 88,000 mg/L, 20% extraction up to about 77,000 mg/L. The range of RO could be extended with newer 1500 psi membranes. A multi-stage process such as NF + RO is required above 1500 psi, but could be used at lower pressure.**

in part a function of the complex behavior of activity coefficients at high ionic strength. A thermodynamic model such as ours is required to be able to evaluate such effects. This is also true in regard to potential effects such changes in pH, which may be significant for some brines.



**Figure 15. Predicted CO<sub>2</sub> pressure in residual brine as a function of water removal due to reverse osmosis at 50°C in a batch system. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site. Note the nearly two order-of-magnitude difference in the scale of the pCO<sub>2</sub> for the two cases.**

In general, we conclude that the potential for freshwater extraction can be approximately categorized as follows:

- 10,000–40,000 mg/L TDS: Standard RO with  $\geq 50\%$  recovery
- 40,000–85,000 mg/L TDS: Standard RO with  $\geq 10\%$  recovery; higher recovery possible using 1500 psi RO membranes and/or multi-stage incremental desalination likely including NF (nanofiltration)
- 85,000–300,000 mg/L TDS: Multi-stage process (NF + RO) using process design that may differ significantly from seawater systems
- 300,000 mg/L TDS brines: Not likely to be treatable

Brines in the 10,000-85,000 mg/L TDS range appear to be abundant (geographically and with depth) and could be targeted in siting CCS operations.

This analysis is subject to further refinement. Many oil field brines contain minor petroleum components that would require removal in pre-treatment prior to desalination. Such factors could significantly tip the cost issue for a given well. It may be possible to manage brine production wells to minimize this factor, either by choice of sequestration site, exact production well site, or choice of production depth. Some potential mineral scaling issues may also have to be addressed, but these may be relatively minor (see the discussion on reduced iron and manganese in the following section).

## **PRELIMINARY COSTS ESTIMATES FOR WATER DESALINATION**

We have carried out preliminary cost estimates for the desalination of saline formation fluids obtained from CO<sub>2</sub> sequestration sites. Because specific carbon capture and storage (CCS) sites have not yet been identified, we have focused our analysis on a generic case for desalination of what we offer as a representative fluid similar to sea water in salinity. Our proposed process takes advantage of the pressurization of the field caused by CO<sub>2</sub> injection to drive desalination using reverse osmosis (RO). This is a major advantage because energy costs for sea water desalination using RO can be 50% or more of the total cost.

### **Reverse Osmosis: Desalination of saline aquifer waters vs. sea water**

Reverse osmosis is a membrane-based desalination process. It uses a microporous polyamide membrane that is permeable to water, but does not allow passage of salt (ions). The solution to be desalinated is placed on one side of the membrane and then pressurized. The pressure drives water across the membrane but leaves most of the dissolved salt behind. The pressure used to



drive the process is equal to the osmotic pressure plus an additional “driving” pressure to cause water to flow in a direction opposite to that of the osmotic pressure gradient, thus the term reverse osmosis. The process is generally carried out in a spiral-wound tubular geometry in order to achieve a large membrane surface area in a small volume. It also allows convenient replacement of fouled or aging membrane modules.

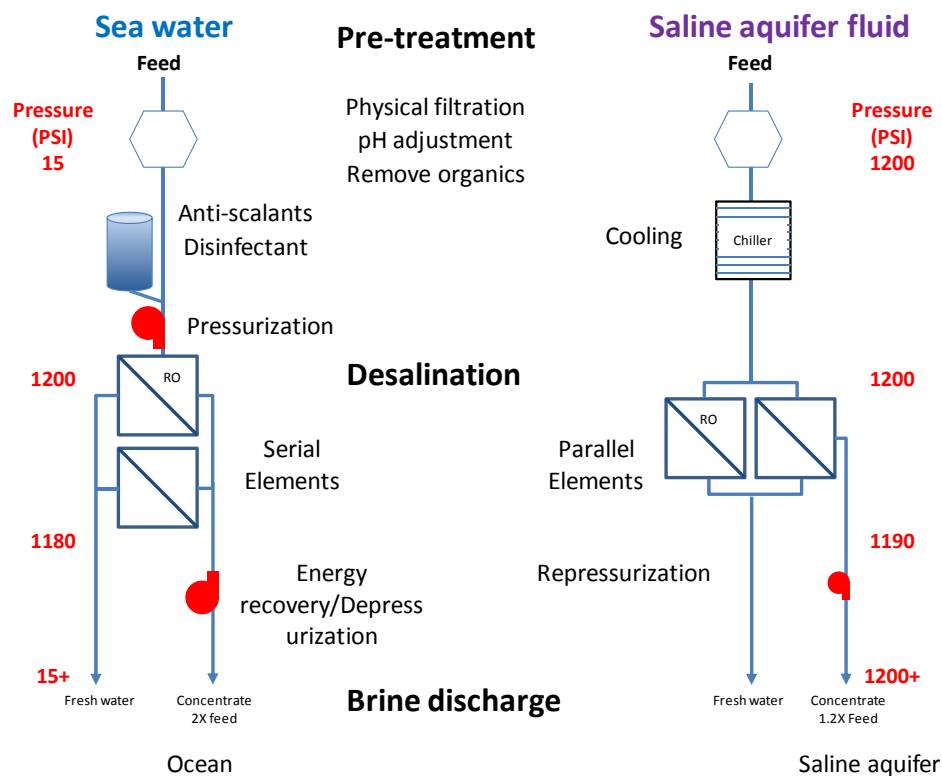
Desalination of sea water using reverse osmosis is a fairly mature technology. Figure 16 shows a schematic of the process, which consists of three main steps:

1. Pre-treatment of the feed using one or more of physical filtration, coagulation, chemical sterilization, and contact with granular activated carbon (GAC)
2. Reverse osmosis
3. Permeate storage and distribution

The reverse osmosis step is often carried out in two or three stages at successively higher pressures, the goal of which is to maximize water recovery. Each stage extracts additional fresh water from the residual brine provided from the previous stage. The operating pressure and membrane types of each stage are optimized for the salinity of the water being processed.

Seawater is similar in composition worldwide, varying only about  $\pm 10$  to 15% in total dissolved solids (TDS), with the relative concentrations of components remaining essentially the same. The major exceptions to this generalization are the biologically-affected components such as calcium, silica, and phosphate. These species are incorporated into living organisms in sea water and so are affected on a local scale by the extent of biological activity.

Because of the uniformity of sea water composition, design of reverse osmosis (RO) seawater systems are similar for most applications, with the major influencing factors being feed temperature and feed water quality with respect to organic and suspended solids concentrations, which are a function of the feed source. If possible, open-ocean intakes are avoided due to entrainment of organic matter and microorganisms. Instead, intake systems that take water from wells drilled into beach sand are used to filter out much of these materials that would otherwise necessitate extensive pre-treatment in order to avoid membrane fouling. Bio-film fouling is especially problematic for RO membrane desalination because the chemicals commonly used to kill micro-organisms, such as chlorine and ozone, will damage the polyamide layer on RO membranes. These compounds cannot be used up-stream from the RO units unless they are subsequently scrubbed from the fluid prior to contact with the membranes.



**Figure 16. Schematic comparison of desalination of seawater vs. desalination of saline formation waters.**

In contrast, reservoir fluids are diverse in composition due to the variety of subsurface interactions they have experienced and rock types they have contacted. Although most pore fluids in sedimentary rocks started as sea water, their compositions have been altered by reactions with rocks, biological activity, and mixing with other fluids. As a result, reservoir waters vary in TDS, pH, amounts of dissolved species such as reduced iron and manganese (not commonly present in surficial oxidized waters), relative amounts of hardness (Ca +Mg) to alkalis (Na +K), alkalinity, and dissolved gases (see discussion in the geochemistry section). The design of systems to desalinate such waters has to adapt to this variability, making some reservoir waters acceptable for standard or modified sea water RO treatment, while other fluids are unsuitable for such processing. As has been described above in the geochemistry section, saline formation waters ranging in TDS from 10,000 mg/L to 60,000 mg/L can be considered for reverse osmosis treatment using a modified sea water process.

Figure 16 shows how the saline aquifer process differs from the standard sea water process. The major differences are:

1. The need for a heat-exchanger (chiller) prior to membrane treatment to cool the fluids to the working range of standard water treatment components ( $<60^{\circ}\text{C}$  or  $140^{\circ}\text{F}$ )
2. Less need for filtration and pre-treatment due to the better quality of fluid in terms of total suspended solids (TSS) and less biological/organic matter
3. Lack of need for a high-pressure pump to pressurize the feed water

One very beneficial factor for RO treatment of reservoir waters is that this water leaves the well head under relatively high pressure, which is typically equal to or higher than that required for seawater membrane processing. Pressurization of seawater feed is a major and very costly component of seawater desalination. With the reservoir water already at high pressure, this costly capital and operating component is thus eliminated for a reservoir RO treatment process. On the other hand, the piping used to bring the fluid from the well head to the desalination plant, and the pre-treatment equipment must all be capable of safely containing this high pressure.

While waters with a TDS  $> 60,000$  mg/L may be amenable to membrane desalination, the process would require nanofiltration pretreatment system for the removal of hardness and a portion of the salinity (monovalent ions). The permeate from the NF step, still under high pressure, would then be fed to a modified seawater RO system as described in this report. The total amount of reservoir water recovered via a NF + RO process would be equivalent to that of the lower recoveries described below. i.e.  $< 25\%$ .

The downside of such a combination membrane system and the reason not to employ it for lower TDS feed waters is its increased capital and operating cost as well as complexity of operation. The technical and cost evaluation of the NF – RO concept is beyond the scope of this study, but may be included in subsequent work.

### **Detailed Desalination System Description**

As previously described, a membrane based reservoir fluid desalination system would be similar to a conventional seawater RO desalination plant, with the major exception that it would be devoid of the feed delivery and high pressure pumping systems. The latter comprises one of the costliest components and longest lead items of this equipment. With no high pressure pumping and the need to return the concentrate under the highest pressure possible for reinjection, another expensive component in the form of an energy recovery device will also not be needed.

The remaining equipment of the reservoir fluid treatment plant will be similar in nature to that of a conventional seawater desalination system. Pressure vessels and membranes, the other costly portion of such plants, will be of the same type and configuration. In order to maximize recovery, operating pressures will be equivalent to that of the high end seawater operations.

One area of difference between the two processes is that the design of seawater systems views the amount of feed strictly from an economic point of view. With an unlimited supply of makeup water available, the amount of water used and returned to the sea is optimized to serve the design of the plant. The only treatment product of value is the extracted permeate water. Conversely, in reservoir water processing, the goal is to extract as much water as possible from the formation and to return as little as possible for deep well injection. As such, the design goals for the two applications differ. The chief difference in operation is that for saline aquifer fluids, it is less desirable to reach high water recoveries, and single-stage low recovery systems are much more attractive. Low recovery allows the use of lower pressures, single staged RO, and less pre-treatment because membrane scaling and fouling issues become more severe with higher water recoveries.

### Saline Formation Water vs. Conventional Seawater Desalination

Table 1 lists the detailed differences between saline formation water and conventional seawater desalination systems.

**Table 1. Conventional Seawater vs. Saline Formation Water RO Treatment Systems.**

| RO System Major Component / Items         | Conventional SW Systems   | Reservoir Treatment System  |
|---|---|---|
| <b>EQUIPMENT</b>                          |   |   |
| High pressure feed piping                 | Only necessary after the high pressure pump   | Starting from the well head   |
| High pressure reject piping               | Only to back pressure control valve, i.e. skid boundary                                     | Return line to the deep well injection point  |
| Intake / feed structure                   | Open intake structure or sea wells  | Reservoir wells   |
| Pretreatment system                       | Multi-media filter or micro-filter  | Activated carbon filter   |
| Feed pumping system                       | Needed from feed source to RO skid  | Not needed - Use well head pressure   |
| Pretreatment system                       | Cartridge filters   | Cartridge filters   |
| Heat exchanger                            | Sometimes used to raise feed temperature in cold environs                                   | To reduce feed temperature to 45°C  |
| Chemical Injection system – bio control   | Yes – for bio control followed by reducing agent  | Not needed  |
| Chemical Injection system – scale control | Yes – scale inhibitor for calcium carbonate   | Yes – scale inhibitor for calcium carbonate and/or calcium sulfate                  |
| High pressure pump                        | Yes (most costly item of RO skid)   | No - Use well head pressure   |
| Energy recovery device                    | Yes – typically used for larger systems   | No – keep reject at maximum pressure for reinjection                                |
| RO pressure vessels (PV)                  | Same for equal permeate capacity  | Same for equal permeate capacity  |
| RO membranes                              | Conventional seawater membranes   | Conventional seawater membranes   |
| Array – configuration                     | Single pass<br>Typically 7 elements per PV for large systems                                | Single pass<br>7 elements per PV  |
| Percent recovery                          | Ranges between 30 to 50%, depending on seawater concentration, system size and energy costs | Ranges between 15 to 45%, depending on reservoir feed concentration and composition |
| System I&C                                | Similar to reservoir system   | Similar to seawater system  |
| MCC/VFD                                   | Includes electrical supply for high HP pump(s)  | Same as conventional SW system, with exception of the high HP pump(s), i.e.         |

|  |  |   |
|--|--|---|
|  |  | no VFD needed   |
| Valves, controls & Instrumentation                 | Similar to reservoir system  | Similar to seawater system, except high pressure pump associated valving and controls   |
| Tanking  | Similar to reservoir system  | Similar to seawater system  |
| Deep well injection                                | Reject typically goes to seawater outfall                                  | Deep well injection required  |
| Civil works  | Very site dependent  | Very site dependent   |
| <b>OPERATIONS</b>                                  |  |   |
| Operating  | Similar to reservoir system except no deep well injection                  | Similar to seawater system except no high pressure pump(s) and energy recovery, but use of deep well injection for reject concentrate |
| Energy consumption                                 | Energy to deliver feed to high pressure pumps and then raise to ~ 1000 psi | Similar to seawater system without the feed and process pumping. Deep well injection pumping energy required.                         |
| Chemicals consumption, including membrane cleaning | Similar to reservoir system  | Similar to seawater system  |
| Maintenance as % of capital                        | Similar to reservoir system  | Similar to seawater system  |

A reservoir water RO desalination system would consist of the following major components:

1. High pressure piping from the well head to the treatment system. The piping would require a material quality of 316L or better to minimize corrosion.
2. RO pretreatment in the form of activated carbon to remove possible organics (oil and grease) and other potentially harmful contaminants from the RO feed. Since the cost of activated carbon and multi-media filters are very similar, the cost estimate will apply to either pretreatment option. It must be noted that, unlike conventional filtration systems, these systems will have to accommodate the high feed pressure.
3. Heat exchanger devices to reduce the feed to the maximum RO membrane temperature of about 45°C.
4. Cartridge filter system
5. Chemical injection system for scale inhibitor and potentially other needs
6. RO skids
7. RO seawater pressure vessels
8. RO seawater membranes
9. System instrumentation and control (I&C)
10. System perimeter piping
11. Valves, controls & instruments
12. Forward flush system
13. Clean-in-place (CIP) system
14. Tankage for chemicals and permeate water
15. Repumping station for reject (concentrate) deep well injection
16. Pretreatment system for deep well injection

17. Civil works
18. Equipment housing – building
19. Installation of equipment
20. Costs include one spare RO train for standby assurance.

Not included was the cost of land acquisition.

Operating and maintenance costs were estimated based on the following cost factors:

1. Consumables, i.e. chemicals, filter replacements, etc.
2. Disposal of hazardous wastes.
3. Filter media replacement.
4. RO membrane replacement; depreciation ranging over two (2) to four (4) years, depending on the percent recovery of the system.
5. Man-hours for supervisor/engineer, operators and technician. Salaries estimated with an overhead factor of two (2).
6. Maintenance, estimated at 3% of capital annually.

The capital and operating costs were analyzed for a number of different system sizes and recoveries as follows:

- RO system sizes measured in permeate capacities: 2, 4, 6 and 8 million gallons per day (mgd).
- Base models for costing were developed for 2 and 4 mgd systems, which were then used to estimate the costs for the 6 and 8 mgd facilities, using exponential escalation factors for subsystems.
- Elements, vessels, and piping were estimated by actual cost and quantity or in the case of piping per pound costs for calculated pipe diameters and thickness.
- RO costs were estimated at 45%, 40%, 35%, 30%, 25% and 15% percent recoveries (defined as percent permeate extracted from the feed).

As noted previously, percent recovery is a function of the incoming feed salinity. Since processing ceiling is dictated by the maximum allowable membrane operating pressure, the osmotic pressure of the reject stream becomes the limiting factor. The higher the feed salinity the lower the percent recovery before the maximum allowable pressure is reached. Operating pressure is comprised of the osmotic pressure of the concentrate plus the hydraulic pressure loss created by the membrane barrier plus a driving pressure to push water through the membrane at a

reasonable rate. At a feed TDS of 60,000 mg/L, recovery may be limited to 15 to 20% recovery. For today's state-of-the-art seawater membranes, the maximum operating pressure is 1,200 psi.

### Criteria for Selection of Optimum Water Recoveries

Recovery is defined as the percent permeate that is extracted from the feed water, which for seawater systems typically ranges from 30% to 50%, depending on feed salinity, size of system, feed temperature, energy costs and the presence of an energy recovery device. Most RO system designers strive to achieve the highest recovery operation possible, which usually minimizes energy and capital costs. Energy costs may make up over 50% of the fixed operating costs in typical seawater RO systems. In reservoir fluid applications, where the feed is delivered under pressure, the cost of energy is not a factor either from the high pressure feed pump or an energy recovery system perspective. This means that operation at less than maximum recovery is much more economically feasible than with conventional systems. However, the capital cost of the associated wells, cooling systems, and piping is inversely proportional to recovery, suggesting optimization of the recovery rate versus required pressures and scaling and fouling risks need to be conducted for each candidate reservoir.

The potential for relatively economic low recovery operation insures that water can be recovered from the reservoir under almost any conditions. At recoveries of 15% or less, coupled with the very low inherent system residence time, almost any of the reservoir waters under 100,000 ppm can be effectively processed at reasonable operating economics. In addition, if one considers the flow profile of typical seawater systems, one quickly realizes that the first element in the vessel typically operates at much higher flux rates, say 20-30 GFD (Gallons per square Foot per Day), than the overall system average, typically 10 GFD or less. This suggests that low recovery operations can be achieved with fewer membrane elements than similar high recovery systems.

45% recovery or higher is feasible for the more dilute waters ranging up to approximately 35,000 mg/L. Waters with 60,000 mg/L or higher feed will most likely be limited to 25% or lower recovery. Newly developed RO membranes are capable of higher operating pressures, up to 1500 psi, but there is limited experience in these pressure ranges with spiral wound membranes. Due to the lack of operational experience with these membranes in larger scale operations, they were not included in this cost analysis.

Aside from the feed water salinity dictating the maximum realistic recovery, there are also some other factors to consider. One is the size of the pretreatment system. For a given permeate output, the percent recovery also fixes the size of the feed piping, the pretreatment system and the brine concentrate returned for deep well injection. Considering that both the high pressure feed piping as well as the reject return piping and subsequent deep well injection are costly items, a maximum percent recovery would be in order.

A contrary argument to the above is that the higher the recovery, the higher the membrane fouling potential, translating to a higher cleaning (CIP) frequency and typically the shorter the membrane life. In view of the overall cost of equipment and operation, these factors are, however, of lesser significance and will typically be trumped by the goal of maximum recovery.

Both the size of the feed piping as well as the penalty of more frequent cleaning and a shorter membrane life is captured in the cost analysis, as is the cost of repressuring the reject for deep well injection.

Not included in the analysis are the potential issues associated with potential hydrological process impact of the injection of a more vs. a less concentrated brine into a specific subterranean formation. Such determination and limitation depends mainly on the receiving geological strata and thus varies from site to site. In this study, it is, therefore, assumed that deep well injection of slightly undersaturated or precipitation inhibited brines is possible. Further work using reservoir simulators to consider the effects of saline fluid removal on reservoir physical properties is needed to address this issue.

#### **Reduced Species: Iron and Manganese**

Depending on the reservoir characteristics, iron and manganese in their reduced states may be present. Since, under normal seawater or RO applications, the feed water is aerated, such metals are typically dealt with by oxidation and removal prior to RO treatment. Since oxidation and subsequent metal removal in a closed, high pressure system is undesirable and unnecessary, the metals will be maintained in their reduced state by isolating them from oxidizing conditions as they pass through the RO membranes.

As divalent ions, iron and manganese will be highly rejected by the membranes so that they will be retained in the reject stream and will subsequently be deep well injected for ultimate disposal. Care will have to be taken to maintain reducing conditions within the entire feed, reject and deep well systems. Some chemical addition in the form of bisulfite may be warranted if there is a danger of oxidation due to atmospheric contact during the repumping operation. With greater than 99.7% membrane rejection of divalent ions, the permeate will be essentially free of these metals so that oxidizing conditions will not be a factor for the permeate water.

#### **Reservoir Water vs. Seawater Pretreatment.**

Pretreatment of seawater for RO processing varies, depending on the feed water source. The pretreatment may consist of simple cartridge filtration and some chemical addition in case of sea wells to more elaborate filtration and chemical conditioning when open seawater intake structures are in use. Some pretreatment may include a variety of intake screens, media filtration



and sometimes micro filtration to ensure proper suspended solids removal from the feed. Intake structures for large seawater systems often consist of costly civil works. Activated carbon treatment is typically not necessary for seawater systems since oil and grease are typically not a factor, unless located at very polluted sites.

The reservoir fluid on the other hand, should contain no suspended solids or turbidity issues, but usually include low levels of organics in the form of oils from subterranean strata. The presence and level of such contaminants will vary from well to well. The generic pretreatment approach for reservoir water will, therefore, consist of activated carbon filters, which will facilitate the removal of not only organics, but also some heavy metals and possibly hydrogen sulfide. Depending on the calcium carbonate or calcium sulfate saturation level of the feed, chemical addition in the form of scale inhibitors will be needed as a prudent precaution. Cartridge filters are always used as a standard pretreatment for RO membrane systems, although in this application, they are less critical compared to convention RO systems since there is no pump to protect.

### **Cooling of Reservoir Feed Water**

Reverse osmosis membranes are typically limited to a maximum operating temperature of 45°C. While “high temperature”, spiral wound, polymeric RO membranes do exist, they are typically of a specialty nature and are not commercially available for seawater use at this time. For large purchases, special high temperature seawater membranes may be available, but would surely be more costly. Even at that, about 80°C would be the temperature limit for such membranes, which, for most reservoir applications, would still pose a feed temperature reduction requirement.

Since the estimated temperature for most reservoir feeds exceeds 100°C, heat exchangers will be necessary to bring the feed water within the membrane operating envelope. It is envisioned that heat exchangers, most likely of a shell and tube design due to the high pressures involved, and made of 317L stainless steel or better would be employed in a split stream formation. The material selection will be a function of the chloride and sulfide levels in the reservoir fluid. The split heat exchanger arrangement would cool a portion of the feed using the counter flowing, previously cooled permeate. The second heat exchanger package would treat the remaining hot feed by cooling it with the previously cooled reject.

The inherent heat losses and inefficiencies of this heat transfer arrangement (as exhibited by the approach temperatures) would be supplemented by an auxiliary heat transfer device, which would either be in the form of an air cooled atmospheric exchanger or it would be tied into the power plant cooling system to provide for the additional cooling as needed. For the latter arrangement, surplus cooling capacity from the power plant would be required. While there

would be some pressure losses associated with the passage through the heat exchange system, the pressure drops across exchangers are typically less than 10 psi.

Depending on the receiving geological formation of the deep well injected concentrate, there may be some benefit involved in injecting a cooler brine. The most notable benefit would be the reduction in corrosion potential with lower temperature and a reduction of calcium scaling due to the increase in calcium sulfate solubility with decreasing temperatures. Counter to these benefits would be the decrease in solubility of other salts, but at the concentrations associated with RO processing, this will not be an issue.

In order to minimize fouling of the heat transfer surfaces, it is expected that the heat exchangers will be located after the activated carbon pretreatment system. A spare heat exchanger train may be employed for in-line cleaning if fouling (or scaling) is expected to be a problem.

### **Pressurized Feed and Reinjection Piping Arrangements**

The reservoir water typically leaves the well head at temperatures ranging from 80 to 120°C and pressures exceeding 1000 psig. Any subsequent piping must, therefore, be designed to carry the dilute brine to its destination. Due to the potentially high chloride content of the water, 316L stainless steel must be considered the minimum baseline material of choice. Other components of corrosive potential, like hydrogen sulfide, must be considered on a case by case basis, depending on the type and concentration present. The presence of additional corrosion potential may require the use of higher alloyed materials such as 317L, 2205 or Al6XN.

The cost estimate assumes a piping length from the well head to the RO plant of 125 ft. This length was used under the assumption that the desalination plant would take water from a single point source and that placement of the equipment at this location and proximity is possible.

Under the assumptions stated, the cost for piping is relatively small compared to the overall cost of the system. If such proximity is not possible or desirable, then the cost of greater piping length must be included, by factoring the estimated piping costs by the additional distance.

Considerations for locating the plant further from the well points may include the following:

- Multiple point sources of the reservoir water
- Placement of the equipment and building close to the well head is not possible
- Reinjection of the brine concentrate is more distant
- Proximity to the power plant is desired
- Other limitations

## Levelized Cost Calculation

Using these cost data, in order to effectively compare different systems, a Levelized Cost of Water was computed over the 25 year time frame using methodology analogous to Levelized Cost of Energy computations as published by NREL and the California Energy Commission. See for example Short et al., 1995, *A Manual for the Economic Evaluation of Energy Efficiency and Renewable Energy Technologies* or California Energy Commission, 2007, *Comparative Costs of California Central Station Electricity Generation Technologies*. Essentially this method computes a NPV for the capital and operating costs over the period at the assumed discount rate. On the production side, the NPV of the production rate per year over the period is also computed. The cost divided by the NPV of production gives the Levelized Cost of Water (LCOW).

$$LCOW = \frac{\text{Initial Investment} + \sum_{t=1}^n \frac{\text{Investment}_t + O \& M_t}{(1 + Disc)^t}}{\sum_{t=1}^n \frac{\text{Water}_{ac-ft/year}}{(1 + Disc)^t}}, t = \text{year of operation}, Disc = \text{Discount Rate}$$

Another way to consider the LCOW is that the LCOW is the NPV of the “price for water” over the period, which may vary, but which always to equal to the NPV of the O&M plus the initial capital cost.

## Economic Results

Table 2 summarizes the major costs and cost factors employed in developing the system costs.

**Table 2. Major Costs and Cost Factors for RO Treatment Systems.**

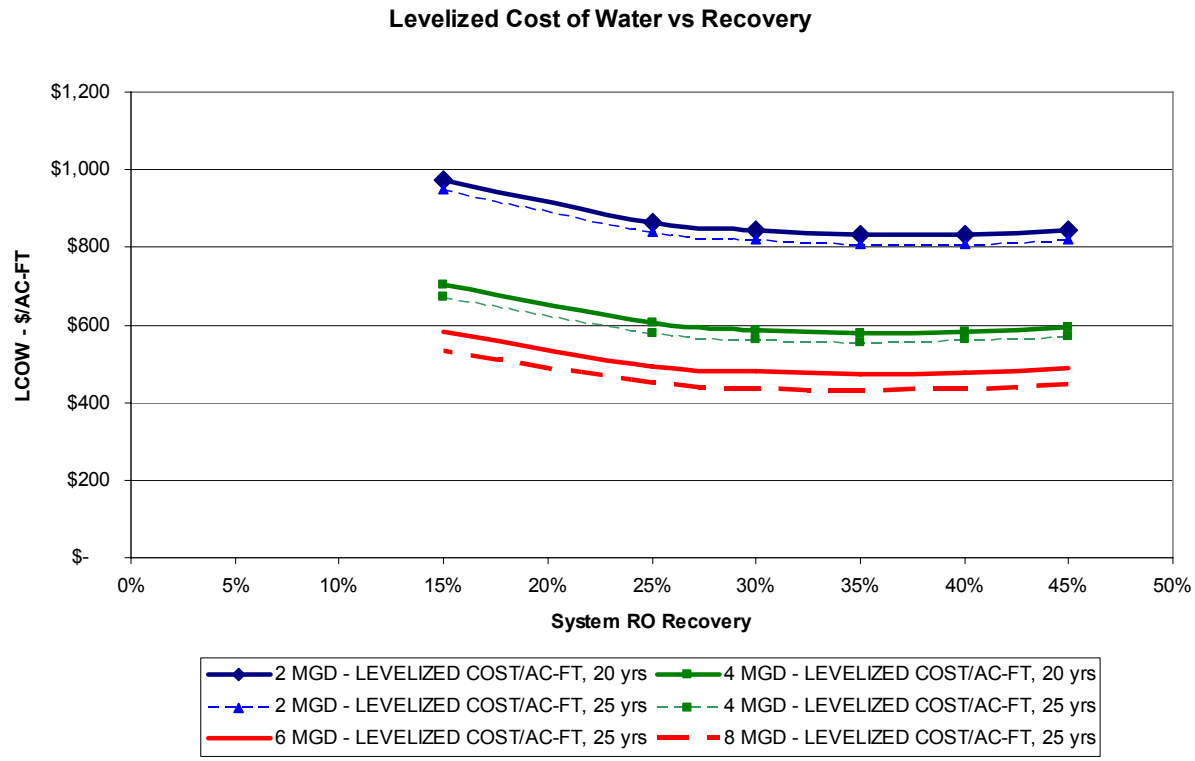
|   |            |                    |
|---|------------|--------------------|
| Assumed Discount Rate                           | 7.00%      |                    |
| Plant Lifetime / Evaluation Period, yrs (20-25) | 25.00      |                    |
| Operating Cost escalation, %/yr                 | 0.00%      |                    |
|   |            |                    |
| Base Operating Pressure at reference conditions | 1,200      | psi                |
| Base recovery                                   | 40%        |                    |
| Cleaning, times/year                            | 0.5        |                    |
| Chemicals                                       | \$3        |                    |
| Consumables                                     |            |                    |
| Activated Carbon                                | \$ 30      | \$/ft <sup>3</sup> |
| Filter cartridges                               | \$ 4       | \$/each            |
| Power, Repressurization                         | \$0.07     | \$/kWh, \$/yr      |
| Power. Misc uses                                | 200.00     | kWh/day, \$/yr     |
| Labor   |            |                    |
| Fringe & Overhead Multiplier                    | 2.00       | factor             |
| Supervisor                                      | \$ 150,000 | Salary             |
| Operators                                       | \$ 60,000  | Salary             |
| Technicians                                     | \$ 75,000  | Salary             |
|   |            |                    |
| Mechanical Maintenance, % of Capital            | 3%         |                    |
| Length of high pressure piping                  | 125        | ft                 |

Results for various scenarios are displayed in the tables and charts below. Figure 17 shows that levelized water costs per acre-foot<sup>1</sup> of permeate vary from about \$450 to \$1000, and that the costs decrease as the size of the operation increases. In addition, there is a most cost effective recovery point (minimum) in plots of recovery vs. cost. This assumes that the water chemistry supports the range of recoveries i.e. the higher recoveries are possible using pressures of less than 1500 psi. Most importantly, however, the lower recovery options are economically close to the higher recovery options – that is the curve is fairly flat. With conventional pumped systems the curve is much more pronounced, greatly favoring higher recovery.

---

<sup>1</sup> One Acre-foot = 325,851 gallons or 1,233 cubic meters

Although we have assumed a fluid salinity similar to that of sea water, our estimated costs are not highly sensitive to salinity. This is because the energy for desalination comes mainly from the existing reservoir pressure field and is not included as an operating costs. In a more conventional desalination system, an increase in salinity makes the process more expensive due



**Figure 17. Levelized cost of water per acre-foot (326,000 gallons) of permeate produced as a function of the water recovery, or fraction of fresh water obtained from the feed.**

**Table 3. Itemization of costs for 2 and 8 MGD (permeate) water desalination plant at 40% water recovery.**

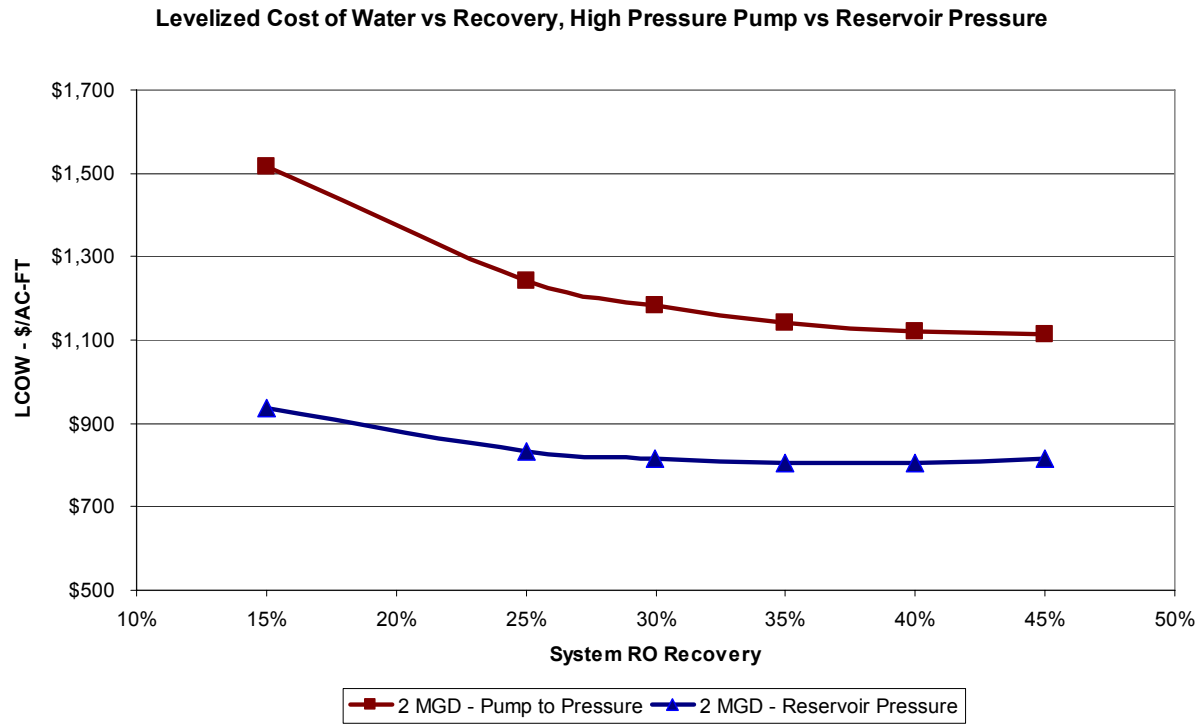
|                                      |      |                   |               |               |               |               |               |               |
|--------------------------------------|------|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Base FEED Flow, MGD                  | 5.00 | Product Flow, MGD | 2.0           | 2.0           | 2.0           | 2.0           | 2.0           | 2.0           |
| Base PRODUCT Flow, MGD               | 2.00 | Recovery, percent | 45.0%         | 40.0%         | 35.0%         | 30.0%         | 25.0%         | 15.0%         |
| Base Recovery                        | 40%  | AC-FT/YR          | 2,240         | 2,240         | 2,240         | 2,240         | 2,240         | 2,240         |
| TOTAL DIRECT OPERATING COSTS         |      | \$/YR             | \$ 1,240,502  | \$ 1,214,833  | \$ 1,200,032  | \$ 1,200,304  | \$ 1,200,168  | \$ 1,283,423  |
|                                      |      | \$/AC-FT          | \$ 553.81     | \$ 542.35     | \$ 535.74     | \$ 535.86     | \$ 535.80     | \$ 572.97     |
| INSTALLED CAPITAL COST, \$/GPD       |      |                   | \$ 3.47       | \$ 3.49       | \$ 3.56       | \$ 3.71       | \$ 3.98       | \$ 4.93       |
| TOTAL DIRECT CAPITAL                 |      |                   | \$ 3,844,576  | \$ 3,912,316  | \$ 4,027,492  | \$ 4,234,852  | \$ 4,588,768  | \$ 5,823,751  |
| INSTALLED CAPITAL COST               |      |                   | \$ 6,934,334  | \$ 6,987,133  | \$ 7,120,062  | \$ 7,414,175  | \$ 7,962,181  | \$ 9,869,483  |
| NPV of O&M                           |      |                   | \$ 14,456,293 | \$ 14,157,162 | \$ 13,984,670 | \$ 13,987,844 | \$ 13,986,263 | \$ 14,956,479 |
| NPV of O&M + Capital Cost            |      |                   | \$ 21,390,627 | \$ 21,144,295 | \$ 21,104,731 | \$ 21,402,020 | \$ 21,948,444 | \$ 24,825,963 |
| NPV of AC-FT/yr                      |      |                   | 26,103        | 26,103        | 26,103        | 26,103        | 26,103        | 26,103        |
| 2 MGD - LEVELIZED COST/AC-FT, 25 yrs |      |                   | \$ 819        | \$ 810        | \$ 809        | \$ 820        | \$ 841        | \$ 951        |

|                                      |       |                   |               |               |               |               |               |               |
|--------------------------------------|-------|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Base FEED Flow, MGD                  | 20.00 | Product Flow, MGD | 8.0           | 8.0           | 8.0           | 8.0           | 8.0           | 8.0           |
| Base PRODUCT Flow, MGD               | 8.00  | Recovery, percent | 45.0%         | 40.0%         | 35.0%         | 30.0%         | 25.0%         | 15.0%         |
| Base Recovery                        | 40%   | AC-FT/YR          | 8,960         | 8,960         | 8,960         | 8,960         | 8,960         | 8,960         |
| TOTAL DIRECT OPERATING COSTS         |       | \$/YR             | \$ 2,251,224  | \$ 2,142,985  | \$ 2,073,988  | \$ 2,061,919  | \$ 2,041,722  | \$ 2,291,636  |
|                                      |       | \$/AC-FT          | \$ 251.26     | \$ 239.18     | \$ 231.48     | \$ 230.13     | \$ 227.88     | \$ 255.77     |
| INSTALLED CAPITAL COST, \$/GPD       |       |                   | \$ 2.58       | \$ 2.59       | \$ 2.62       | \$ 2.72       | \$ 2.92       | \$ 3.67       |
| TOTAL DIRECT CAPITAL                 |       |                   | \$ 10,643,981 | \$ 10,796,811 | \$ 10,996,812 | \$ 11,530,415 | \$ 12,499,362 | \$ 16,138,799 |
| INSTALLED CAPITAL COST               |       |                   | \$ 20,629,930 | \$ 20,756,123 | \$ 20,947,918 | \$ 21,757,741 | \$ 23,349,555 | \$ 29,354,228 |
| NPV of O&M                           |       |                   | \$ 23,849,500 | \$ 22,702,811 | \$ 21,971,857 | \$ 21,844,001 | \$ 21,630,028 | \$ 24,277,624 |
| NPV of O&M + Capital Cost            |       |                   | \$ 44,479,430 | \$ 43,458,933 | \$ 42,919,775 | \$ 43,601,742 | \$ 44,979,583 | \$ 53,631,852 |
| NPV of AC-FT/yr4                     |       | AC-FT/Period      | 94,920        | 94,920        | 94,920        | 94,920        | 94,920        | 94,920        |
| 8 MGD - LEVELIZED COST/AC-FT, 20 yrs |       |                   | \$ 469        | \$ 458        | \$ 452        | \$ 459        | \$ 474        | \$ 565        |

both to the need for more energy to drive a higher pressure pump to overcome increased osmotic pressure, and the need for higher strength materials to contain the higher pressure fluid. For this reason, we believe our estimated costs are fairly representative for the range of fluid salinities for which an essentially conventional RO process can be used (i.e. 10,000-85,000 ppm TDS).

Figure 18 compares the costs for a system using CCS reservoir pressure to drive the RO process, with an identical system that uses high-pressure pumps to drive desalination. The difference between the curves reflects the estimated cost of energy to drive the desalination system.



**Figure 18. Comparison of the levelized costs of water for a saline aquifer fluid for which the pressure is supplied by CO<sub>2</sub> injection, vs. the costs for a conventional system where the pressure is supplied by high-pressure pumps.**

One of the items to warrant further review is the problem of optimizing the front end heat exchanger system used to reduce the reservoir fluid's temperature for RO processing. As briefly described in this document, a cooling device to accomplish the necessary heat reduction will consist of a split heat exchanger arrangement, which will have to be augmented via a secondary heat reduction source. The specific nature of this supplementary heat rejection will have to be considered. The technical and cost impact of coupling the heat reduction with the power plant's cooling system vs. a stand-alone system that uses atmospheric cooling, possibly augmented by spray evaporation, must be made. Since this would consume RO permeate, thereby reducing the amount of recovered water for power plant use, it may be a significant factor to consider.

The high pressure of the reservoir fluid serves as the driving pressure for the RO process and can, therefore, not be compromised. This study addressed the possibilities of using a shell and tube type heat exchanger system to reduce the RO feed temperature and then briefly considered the use of high temperature membranes. Since the RO membrane operating temperature may have a significant impact on the cost of equipment, further study would be warranted to determine the possibility of using different heat rejection devices or high temperature membranes, or a combination of the two.

## PRELIMINARY RESERVOIR MODELING

Using the NUFT code (Nitao 2000a, 2000b), we have conducted preliminary simulations of the effect on the reservoir pressure field of CO<sub>2</sub> injection with and without brine production. NUFT is an LLNL code used to study sequestration flow, transport, and geochemical reactions. Our results for the case of injection with no brine production are qualitatively consistent with previously reported results (e.g., Birkholzer and Zhou, 2009; Birkholzer et al., 2009), which show that the overpressure field expands well out from the body of injected supercritical CO<sub>2</sub>.

A two-dimensional simulation domain, as seen in Figure 19, is selected to represent a 200m-thick reservoir at a depth of about 2000 m. While the top and bottom boundaries are kept impermeable the hydrostatic pressure conditions are assigned along the lateral boundary. The permeability and porosity of the reservoir are assumed as 100 mD and 20%, respectively. The injection well with an area of 1x1 m<sup>2</sup> is located at the top of the formation, and the supercritical CO<sub>2</sub> is injected at a constant rate of 1000 ton/yr-m for 5 years. The injection rate used for these 2-D simulations corresponds roughly to an injection rate of 10<sup>6</sup> ton/yr through a 1000 m-long horizontal injection well. The water pumping well is placed at the bottom of the reservoir and two km laterally apart from the injection well. The water extraction rate is chosen as the same as the injection rate.

Figure 20 and

Figure 21 show the comparison of pressure and liquid saturation profiles at 5 years after the injection starts for the cases with and without brine pumping/extraction. It can be seen that water extraction readily helps to reduce the peak overpressure from ~65 bars to ~34 bars. It should also be noted that due to the pumping/extraction effects there is a tendency for the CO<sub>2</sub> plume to migrate towards the pumping well especially when the injection and production wells are placed closer to each other.

There are a number of reservoir modeling issues that remain to be addressed, such as the optimum number and configuration of wells (which must include at least one residual brine reinjection well) and associated rates of injection and production. A brine production well (which tends to produce a surrounding field of underpressure) must be emplaced so as to have a beneficial effect on the overall pressure field, but cannot be so close that injected CO<sub>2</sub> migrates into it. A brine reinjection well will tend to produce a surrounding field of overpressure, the effect of which also needs to be analyzed. Migration of residual brine to a brine production well needs to be avoided. There is also the question of the effect of limiting formation overpressure on preventing leakage from the storage formation and on controlling unwanted geomechanical effects. These issues will be explored in more detail in the coming year.



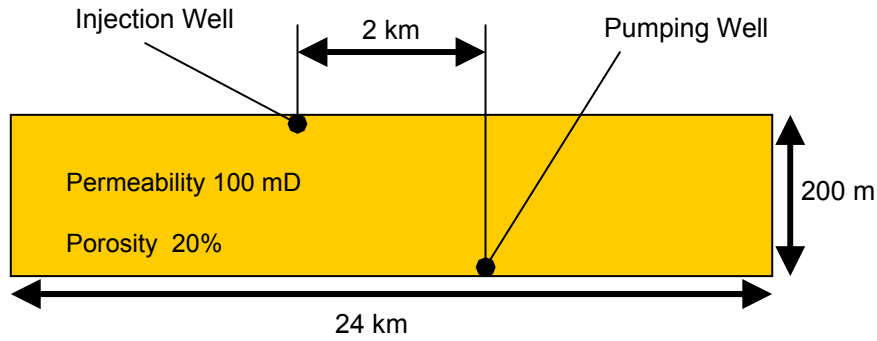


Figure 19. Two-dimensional model domain and geometry used in preliminary reservoir pressure analysis.

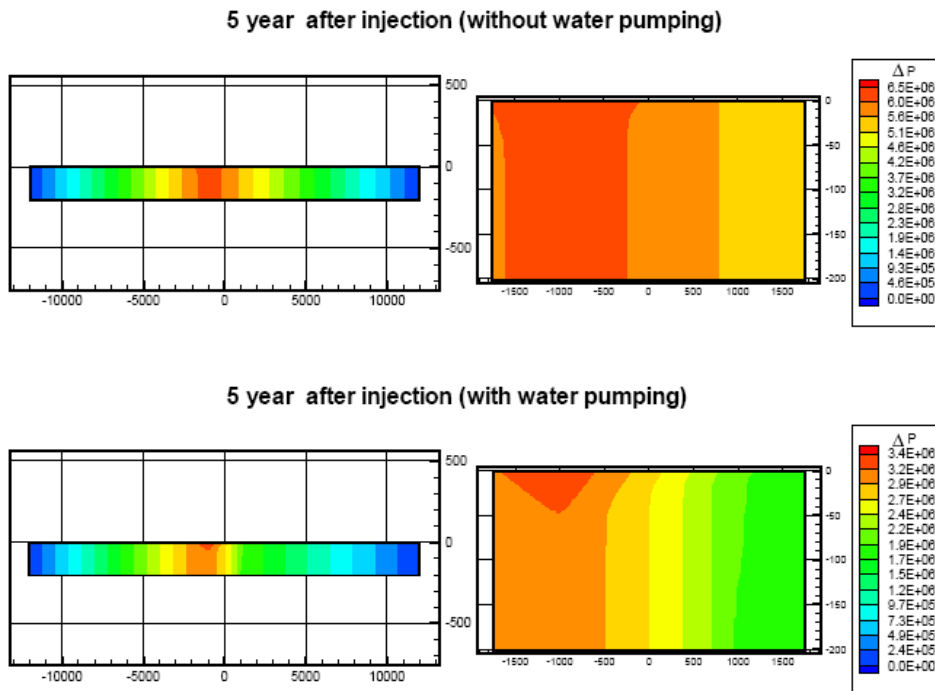
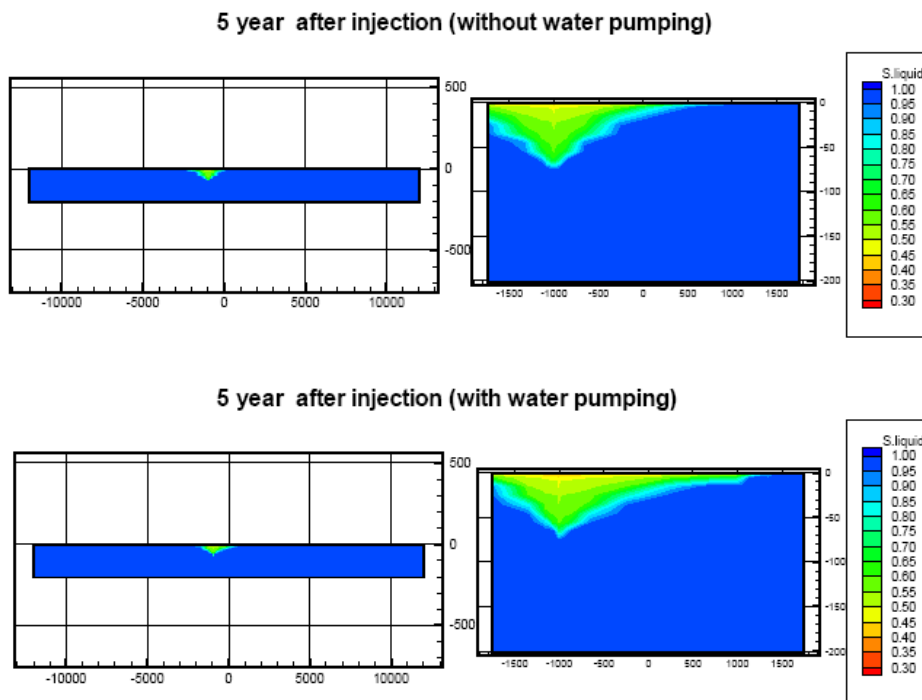


Figure 20. Pressure profile at 5 years after injection for the cases with and without water pumping/extraction



**Figure 21. Liquid saturation profile at 5 years after injection for the cases with and without water pumping/extraction.**

## CONCLUSIONS

Our initial conclusions are encouraging.

Many saline formation waters such as those found in Wyoming are amenable to conventional or largely conventional RO treatment. We have looked at Na-Cl brine from the Nugget Formation at the Big Sky Carbon Sequestration Partnership site in Sublette County, Wyoming. Here 7.5-24% removal with conventional RO is realistic; higher removal appears achievable with NF. The lower TDS Na-Cl-SO<sub>4</sub> brine from the underlying Tensleep Formation would support >80% removal with conventional RO.

Brines from other proposed sequestration sites can now be analyzed readily using our thermodynamic model. An accurate osmotic pressure curve appropriate to these brines can be used to evaluate cost and equipment specifications. Next year we will consider more of the United States CSP site brines as analyses from Phase 3 operations become available.

We have examined a range of saline formation water compositions relevant or potentially relevant to CCS and noted the principal compositional trends pertinent to evaluating the feasibility of fresh water extraction. We have proposed a general categorization for the feasibility of the process based total dissolved solids (TDS):

- 10,000–40,000 mg/L TDS: Standard RO with  $\geq 50\%$  recovery
- 40,000–85,000 mg/L TDS: Standard RO with  $\geq 10\%$  recovery; higher recovery possible using 1500 psi RO membranes and/or multi-stage incremental desalination likely including NF (nanofiltration)
- 85,000–300,000 mg/L TDS: Multi-stage process (NF + RO) using process design that may differ significantly from seawater systems
- > 300,000 mg/L TDS brines: Not likely to be treatable

Brines in the 10,000-85,000 mg/L TDS range appear to be abundant (geographically and with depth) and could be targeted in planning CCS operations.

Costs for desalination of fluids from saline aquifers are in the range of \$400-1000/ acre foot of permeate. This is about half of conventional seawater desalination costs of \$1000-1400/acre foot. The primary reason for the cost reduction relative to sea water is the lack of need for energy to drive the high-pressure pumps to carry out desalination using reverse osmosis membranes. An additional cost savings has to do with less pre-treatment than is customary for ocean waters full of biological activity and their degradation products. An innovative parallel low-recovery

approach is proposed that would be particularly effective for saline formation waters in the 40,000-85,000 mg/L TDS range.

The underlying technical and economic drivers and equipment for reservoir and seawater desalination systems are quite different, further effort is needed to study the feasibility and impact of operating RO systems at very low recoveries to accommodate some of the high TDS feed waters. The benefit of removing water from the reservoir and recovering it for power plant use in remote and arid regions may allow a low RO recovery operation, which would be unthinkable for brine or seawater desalination.

The possibility of using an NF + RO has been briefly addressed. This membrane treatment approach would use the NF membranes to soften and partially desalinate reservoir waters of high TDS (>85,000). This reasonable approach needs a more rigorous technical review and an analysis to evaluate its economic merit.

Withdrawing pressurized brine can have a very beneficial effect on reservoir pressure (helping to avoid leakage and undesirable geomechanical effects), while increasing total available storage capacity. We have conducted preliminary calculations of the evolution of the pressure field that develops in an injection formation, with and without the presence of a brine production well. The brine production well was shown to substantially reduce the maximum overpressure.

A number of reservoir modeling issues remain to be addressed, such as the optimum number and configuration of wells (which must include at least one residual brine reinjection well) and associated rates of injection and production. A brine production well must be emplaced so as to have a beneficial effect on the overall pressure field, but cannot be so close that injected CO<sub>2</sub> migrates into it. A brine reinjection well must also be considered, as it will affect the overall pressure field and opens the possibility of migration of residual brine to a brine production well. There is also the issue of quantifying the effect of limiting formation overpressure on preventing leakage from the storage formation and on controlling unwanted geomechanical effects. These issues will be explored in more detail in the coming year.

## **ACKNOWLEDGMENTS**

We thank Geoffrey Thyne (Enhanced Oil Recovery Institute, University of Wyoming) and George Breit (U.S. Geological Survey, Denver) for helpful discussions about produced waters.

## REFERENCES

- Bechtel SAIC Company. 2007. *In-Drift Precipitates/Salts Model*. ANL-EBS-MD-000045 REV 03. Bechtel SAIC Company, Las Vegas, Nevada.
- Birkholzer, J.T., and Zhou, Q. 2009. Basin-scale hydrogeologic impacts of CO<sub>2</sub> storage: Capacity and regulatory implications. *International Journal of Greenhouse Gas Control*, v. 3, p. 745-456.
- Birkholzer, J.T., Zhou, Q., and Tsang, C.-F. 2009. Large-scale impact of CO<sub>2</sub> storage in deep saline aquifers: A sensitivity study on pressure response in stratified systems. *International Journal of Greenhouse Gas Control*, v. 3, p. 181-194.
- Breit, G.N. 2002. *Produced Waters Database: U.S. Geological Survey provisional database*. Downloadable from: <http://energy.cr.usgs.gov/prov/prodwat/index.htm>.
- California Energy Commission. 2007. *Comparative Costs of California Central Station Electricity Generation Technologies*. CEC-200-2007-011-SD. California Energy Commission, Sacramento, CA. Downloadable from: <http://www.energy.ca.gov/2007publications/CEC-200-2007-011/CEC-200-2007-011-SD.PDF>.
- Dow Water Solutions. 2009. FILMTEC™ Reverse Osmosis Membranes Technical Manual. Form No. 609-00071-1009. Dow Water Solutions, Midland, MI. Downloadable from: <http://www.dow.com/liquidseps/lit/techman.htm>.
- Greenberg, J.P. and Møller, N. 1989. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system to high concentration from 0 to 250°C. *Geochimica et Cosmochimica Acta*, v. 53, p. 2503–2518
- Kharaka, Y.K., Berry, F.A.F., and Friedman, I. 1973, Isotopic composition of oil-field brines from Kettleman North Dome, California, and their geologic implications. *Geochimica et Cosmochimica Acta*, v. 37, p. 1899-1908.
- National Energy Technology Laboratory. 2005. *Rock Mountain Basins Produced Water Database*. National Energy Technology Laboratory, Pittsburgh, PA. Downloadable from: <http://www.netl.doe.gov/technologies/oil-gas/Software/database.html>.
- Nitao, J.J. 2000a. *Reference Manual for the NUFT Flow and Transport Code, Version 3.0*. UCRL-MA-130651-REV-1. Lawrence Livermore National Laboratory, Livermore, CA.

- Nitao, J.J. 2000b. *User's Manual for the USNT Module of the NUFT Code, Version 3.0 (NP-Phase, NC-Component, Thermal)*. UCRL-MA-130653-REV-2. Lawrence Livermore National Laboratory, Livermore, CA.
- Pabalan, R.T. and Pitzer, K.S. 1987. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO<sub>4</sub>-OH-H<sub>2</sub>O. *Geochimica et Cosmochimica Acta*, v. 51, p. 2429-2443.
- Pitzer, K.S. 1991. Ion Interaction Approach: Theory and Data Correlation. Chapter 3 of *Activity Coefficients in Electrolyte Solutions*, 2nd Edition. Pitzer, K.S., ed. Boca Raton, Florida: CRC Press.
- Short, W., Packey, D.J., and Holt, T. 1995. *A Manual for the Economic Evaluation of Energy Efficiency and Renewable Energy Technologies*. NREL/TP-462-5173. National Renewable Energy Laboratory, Golden, CO. Downloadable from: <http://www.nrel.gov/csp/troughnet/pdfs/5173.pdf>.
- Thomsen, K. 1997. *Aqueous electrolytes: model parameters and process simulation*. Ph.D. thesis, Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark. Downloadable from: <http://kth.ivc-sep.dk/Thesis%20k%20thomsen%201997.pdf>.
- Thomsen, K. 2005. Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model. *Pure and Applied Chemistry*, v. 77, p. 531-542.
- Wolery, T.J., and Jarek, R.L. 2003. Software User's Manual, EQ3/6, Version 8.0. Civilian Radioactive Waste Management System Management & Operating Contractor. 10813-UM-8.0-00. Prepared for U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Las Vegas, Nevada.